

NEW ANALYTICAL METHODS FOR DETERMINING TRACE ELEMENTS IN COAL

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ABSTRACT

New and improved analytical methods, based on modern spectroscopic techniques, have been developed to provide more reliable data on the levels of environmentally significant elements in Australian bituminous thermal coals. Arsenic, selenium and antimony are determined using hydride generation atomic absorption or fluorescence spectrometry, applied to an Eschka fusion of the raw coal. Boron is determined on the same digest using inductively coupled plasma atomic emission spectrometry (ICPAES). ICPAES is also used to determine beryllium, chromium, cobalt, copper, manganese, molybdenum, nickel, lead and zinc, after fusion of a low temperature ash with lithium borate. Other elements of concern including cadmium, uranium and thorium are analysed by inductively coupled plasma mass spectrometry on a mixed acid digest of a low temperature ash. This technique was also suitable for determining elements analysed by the ICPAES. Improved methods for chlorine and fluorine have also been developed. Details of the methods will be given and results of validation trials discussed on some of the methods which are anticipated to be designated Australian standard methods.

INTRODUCTION

Increasing attention is being focussed on the potential environmental impact of trace elements, particularly those of environmental concern, associated with electricity production from coal-fired power plants. As a consequence the impact of trace elements on the surrounding ecology from atmospheric emissions and mobilisation in ash dams is coming under increased scrutiny.

Trace elements of concern to the environment and health have been identified by the United States National Research Council¹. More recently the levels of trace elements in coal have received greater attention with the introduction of legislation, in some countries, which imposes atmospheric discharge limits on a range of environmentally sensitive trace elements. Details of these limits in Australia, Austria, Germany, Italy and the United States of America are given by Clarke and Sloss². Of most significance relating to the impact of trace elements on the environment was the recent amendments to the US Clean Air Act, 1991, which greatly expanded the role of the US Environmental Protection Agency to regulate trace element emissions. Included in the list of 190 hazardous air pollutants were arsenic, antimony, beryllium, cadmium, cobalt, chromium, chlorine, fluorine, mercury, manganese, nickel, lead and selenium together with radionuclides including radon. Although the power industry is not included in the list of source categories, the amendments require the measurement of mercury emissions from coal-fired power plants. The Electric Power Research Institute (EPRI) in the US has carried out a field monitoring project to measure a range of trace elements in the process and discharge streams of power plants to determine the efficiency of control devices to reduce emissions of air toxics³.

The imposition of stricter controls by regulatory bodies on emissions has focussed attention on the levels of environmentally sensitive elements, particularly those designated as air toxics, in thermal coals. As a consequence of this there is an increasing need to accurately specify the levels of these trace elements to satisfy contractual requirements. Australia is the world's largest exporter of coal and the implications of regulations on trace element emissions are for the development of better quality assurance procedures in the specification of the levels of key environmental trace elements in export thermal coals.

Quality assurance requires the application of validated standard methods which guarantee the accuracy and reliability of the analytical data. The problem is that, in most cases, current standard methods do not have the necessary accuracy to specify the levels of environmentally sensitive trace elements at the concentrations normally present in Australian product thermal coals. One reason for this inadequacy of current standard methods is that they are based on long established analytical techniques such as atomic absorption spectrometry (AAS) which lack the sensitivity to provide the necessary quality assurance. AAS is also a single element technique which, in terms of the number of elements identified as environmentally significant, makes it less cost effective than newer multi-element, simultaneous techniques such as inductively coupled plasma atomic emission spectrometry (ICPAES). Over the past decade this technique has become more readily available in commercial laboratories and its suitability for determining many of the designated trace elements has been established.

In view of the pressing requirements for better quality assurance, new analytical methods based on ICPAES has been developed. The current standard methods based on hydride generation-AAS for arsenic and selenium has been revisited and an improved method, based on atomic fluorescence spectrometry, has provided increased sensitivity for these trace elements. These methods are undergoing validation trials with the anticipation that they will be adopted as new Australian standard methods.

Other techniques have also been used to develop reliable methods. These include inductively coupled plasma mass spectrometry (ICPMS) for a range of trace elements including cadmium, nickel, lead, molybdenum, thorium and uranium. Proton induced gamma ray emission (PIGE) has been applied to the determination of fluorine and X-ray fluorescence spectrometry (XRF) for chlorine.

CURRENT STATUS OF STANDARD METHODS

The performance of current standard methods is shown in table 1 where the lower limits of determination of the methods are compared with the means and range values for the key environmental trace elements in Australian export thermal coals as given by Dale and Fardy⁴. In most cases the current methods are inadequate for determinations at the low range values. For cadmium, cobalt, molybdenum, uranium and thorium no standard methods exist.

Table 1. Mean and Range Values for Trace Elements of Environmental Concern in Australian Export Thermal Coals Compared with Lower Limit of Determination (LLD) of Available Standard Methods

Element	Mean*	mg/kg				
		Range		LLD*		
		Low	High	AS	ASTM	ISO
As	2	<1	7	0.5	1	1
B	17	<5	40	20	-	-
Cd	0.09	<0.05	0.22	-	-	-
Hg	0.06	0.01	0.14	0.01	0.01	-
Mo	1.6	0.25	5.5	-	-	-
Pb	7.5	2.5	13	40	10	-
Se	1	<1	2	-	1	-
Mn	30	3	110	30	-	-
Cr	12	5	27	20	5	-
Cu	12	4	23	50	5	-
Ni	14	<9	39	20	10	-
V	26	10	63	100	10	-
Zn	19	3	53	80	50	-
F	120	40	200	50	10	-
Co	5.3	1.6	14	-	-	-
Cl	200	20	630	100	200	-
Sb	0.54	<0.05	1.5	-	-	-
Be	1.4	0.25	5.5	2	0.5	-
U	1.1	0.3	2.1	-	-	-
Th	3.5	1.1	7.7	-	-	-

* AS - Australian Standard

ASTM - American Society for Testing Materials

ISO - International Organisation for Standardisation

METHOD FOR ARSENIC, SELENIUM AND ANTIMONY

This method is based on the current US standard (ASTM D4606-87) which involves the fusion of the raw coal using Eschka's mixture. The elements arsenic and selenium are determined by hydride generation-AAS using matrix matched standards. The new method uses similar conditions for generation of the hydride. However advantage is taken of the higher sensitivity obtained with atomic fluorescence spectrometry. The method has also been found satisfactory for determining antimony and has been validated by analysis of certified reference materials as shown in Table 2.

Table 2. Results for Arsenic, Selenium and Antimony Obtained on Certified Reference Materials using Hydride Generation Atomic Fluorescence Spectrometry

CRM	Arsenic		Selenium		Antimony	
	mg/kg		Found	Certified	Found	Certified
	Certified	Found				
NIST 1632b	3.70 ± 0.28	3.72 ± 0.12	1.30 ± 0.12	1.29 ± 0.11	0.28 ± 0.02	(0.24)
SARM 19	7.65 ± 0.10	7 ± 1	1.12 ± 0.06	1	-	-
SARM 20	-	-	0.75 ± 0.04	0.8 ± 0.2	-	-

This method is currently undergoing validation tests in an interlaboratory trial and is anticipated to be adopted as an Australian standard method.

METHOD FOR BORON

The method developed is based on the Eschka fusion procedure used for arsenic, selenium and antimony. The element is determined using ICPAES using matrix matched standards. The method was validated using South African reference coals as demonstrated by the following results.

Table 3. Results for Boron Obtained on an SARM Reference Coal

CRM	mg/kg	
	Found	Indicated*
18	28	30
19	94	90
20	84	90

* Values are not certified.

This method is also undergoing validation tests and is anticipated to be adopted as an Australian standard.

ICPAES METHOD FOR TRACE ELEMENTS

This method is based on fusion of a 450°C ash of the coal with a mixture of 1 part lithium metaborate to 3 parts lithium tetraborate. The elements chromium, copper, zinc, vanadium, manganese, nickel, cobalt, molybdenum, lead and beryllium are determined using ICPAES with matrix matched standards.

The method has been validated using NIST 1632b and is currently undergoing validation tests in an interlaboratory trial. It is anticipated to be adopted as an Australian standard method.

TRACE ELEMENTS BY ICPMS

This technique has gained popularity over the past decade because of its very high sensitivity and multi-element capability. It has been applied, in this laboratory, to the determination of a wide range of trace elements in coal. The method developed is based on dissolution of a 450°C ash of the coal using a mixture of nitric-hydrochloric-hydrofluoric acids. The elements are determined using appropriate internal standard elements (indium, thallium and enriched stable isotopes of chromium-53 and zinc-68).

This technique has been found suitable for determining a wide range of environmental trace elements including uranium, thorium, cadmium, antimony, lead, nickel, arsenic, beryllium, chromium, cobalt, copper, zinc, vanadium and molybdenum. Of particular significance is the ability to analyse for cadmium, uranium, and thorium (detection limits 0.01, 0.005 and 0.005 mg/kg respectively). There are no standard methods available for these elements because of their low abundances in coal and the lack of sensitivity of more conventional techniques. Cadmium however could possibly be analysed by graphite furnace-AAS.

Although ICPMS instruments are expensive the technique is finding increased popularity in commercial laboratories. It is expected that its application to the determination of trace elements

in coal will receive greater attention because of its high sensitivity and multi-element capability which makes it cost effective.

METHOD FOR CHLORINE

Current methods for chlorine are based on oxygen bomb digestion or fusion followed by determination by ion-selective electrode (AS 1038.8.1, ASTM D4208). There are however, recognised problems with these methods. These relate to the recovery of the chlorine during the sample destruction and the lack of sensitivity of the ion-selective measurement. Evidence of the problems has been highlighted in international interlaboratory comparisons such as the CANSPECS program organised by Energy Resources Canada. The extreme variability of results by laboratories using the same standard method suggests that these methods lack the reliability required by standard methods. This variability is of great concern to Australian coal producers because of disputes that occur between suppliers and buyers.

In recognition of the problems with current methods, a procedure is being developed based on X-ray fluorescence spectrometry (XRF). This procedure has the advantage that it analyses the raw coal and is therefore non-destructive thereby overcoming one of the main deficiencies of current methods.

The suitability of the XRF procedure has been verified by comparison with results obtained by instrumental neutron activation analysis (see Table 4). The lower limit of determination of the XRF method is 30 mg/kg which is below the low range value for Australian coals. Analysis of the NIST 1632b CRM gave a value of 1190 mg/kg which compares favourably with the indicated value of 1230 mg/kg. The new method requires minimal sample preparation (grinding to less than 75 μm and the addition of an internal standard) and is cost effective on the basis of its high sample throughput compared to current standard methods.

Table 4 - Comparison of Chlorine Results Obtained on Coals by XRF and INAA

Sample	Cl (mg/kg)	
	XRF	INAA
1	250	235
2	450	410
3	505	495
4	670	610
5	970	1075

METHOD FOR FLUORINE

The standard method for determining this element is based on destruction of the raw coal by pyrohydrolysis followed by determination with an ion-selective electrode (AS 1038.10.4). This method has limitations in that the problems are associated with the liberation of the fluorine from the sample and the rather poor sensitivity of the ion-selective electrode at the levels normally encountered in coals.

The method used in our laboratory is based on proton induced gamma ray emission using the 2MV van der Graaf accelerator available through the Australian Nuclear Science and Technology Organisation. Previous work³ has verified the application of this technique to the analysis of coal for fluorine. It is based on the irradiation of the raw coal with high energy protons in which the fluorine atoms produce characteristic g-rays. It is therefore non-destructive. Analysis of the NIST 1632a CRM gave a mean value of 183 mg/kg with a standard deviation of 10 mg/kg (12 determinations). The accepted value for this CRM is 178 mg/kg. The detection limit is 5 mg/kg.

PERFORMANCE OF NEW METHODS

The new methods provide the necessary sensitivity to meet the requirements for determining a range of key environmental trace elements in Australian coals. This is demonstrated in Table 5 which compares the lower limit of determination of the new methods and the current standard methods. For most elements, the new methods provide the capability for reliably analysing Australian coals at the levels normally present.

Validation trials are currently in progress involving a number of participating commercial laboratories. Preliminary data suggests that the methods for arsenic, selenium and antimony based on the hydride generation-AFS technique will meet the requirements for acceptance as a standard method as required by Standards Australia. Similar agreement between laboratories for

the boron and ICPAES methods suggests that these will become standard methods. Future efforts will be directed towards the establishment of an Australian standard method based on ICPMS which would account for cadmium, uranium and thorium.

The methods used for chlorine and fluorine are presently considered as reference methods. There needs to be a revision of current methods in view of the discrepancies which occur between laboratories.

Table 5 - Lower Limits of Determination (LLD) for Trace Elements with New Analytical Methods Compared with Standard Methods and the Means and Range Values in Australian Export Thermal Coals

Element	mg/kg				
	Mean	Range		LLD	
		Low	High	New Method	Standard Method
As	2	<1	7	0.03	0.4
B	17	<5	40	3	20
Cd	0.09	<0.05	0.22	0.01	-
Mo	1.6	0.25	5.5	0.2	-
Pb	7.5	2.5	13	0.2	10
Se	1	<1	2	0.03	1
Mn	30	3	110	0.02	-
Cr	12	5	27	0.1	5
Cu	12	4	23	0.2	5
Ni	14	<9	39	2	10
V	26	10	63	0.2	10
Zn	19	3	53	0.2	50
Co	5.3	1.6	14	0.2	-
Cl	200	20	650	50	200
Sb	0.54	<0.05	1.5	0.03	-
Be	1.4	0.25	5.5	0.01	-
U	1.1	0.3	2.1	0.03	-
Th	3.5	1.1	7.7	0.03	-
F	120	40	200	20	50

SUMMARY

The new methods provide adequate sensitivity to reliably determine a range of key environmental trace elements in Australian coals. These methods are based on modern instrumentation which is generally available in commercial laboratories. These new methods address the need for better quality assurance in the specification of trace elements in export coals. This has been as a direct result of increasing concern on the environmental impact of trace elements from coal-fired power plants.

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INVESTIGATION OF THE BEHAVIOR OF POTENTIALLY HAZARDOUS TRACE ELEMENTS IN KENTUCKY COALS AND COMBUSTION BYPRODUCTS

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INTRODUCTION

The minor- and trace-element content of coal is of great interest because of the potentially hazardous impact on human health and the environment resulting from their release during coal combustion. Of the one billion tons of coal mined annually in the United States, 85-90% is consumed by coal-fired power plants.¹ Potentially toxic elements present at concentrations as low as a few $\mu\text{g/g}$ can be released in large quantities from combustion of this magnitude. Of special concern are those trace elements that occur naturally in coal which have been designated as potential hazardous air pollutants (HAPs) in the 1990 Amendments to the Clean Air Act.²

The principle objective of this work was to investigate a combination of physical and chemical coal cleaning techniques to remove 90 percent of HAP trace elements at 90 percent combustibles recovery from Kentucky #9 coal. Samples of this coal were first subjected to physical separation by flotation in a Denver cell. The float fraction from the Denver cell was then used as feed material for hydrothermal leaching tests in which the efficacy of dilute alkali (NaOH) and acid (HNO_3) solutions at various temperatures and pressures was investigated. The combined column flotation and mild chemical cleaning strategy removed 60-80% of trace elements with greater than 85% recovery of combustibles from very finely ground (-325 mesh) coal. The elemental composition of the samples generated at each stage was determined using particle induced X-ray emission (PIXE) analysis. PIXE is a rapid, instrumental technique that, in principle, is capable of analyzing all elements from sodium through uranium with sensitivities as low as 1 $\mu\text{g/g}$.

EXPERIMENTAL PROCEDURE

Sample Preparation

A sample of run of mine coal from the Kentucky #9 seam was collected at the mine site, and split into subsamples as needed. Each subsample was then ground to -325 mesh and a 5% (w/v) slurry was prepared. The slurry was subjected to Denver flotation, and the float fraction was employed as the feed sample for hydrothermal leaching using either a NaOH or HNO_3 solution in a 1 liter autoclave reactor. The duration, temperature, and pressure of the chemical leaching process were varied to ascertain their influence, if any, on the removal of trace elements. Each clean coal sample was dried at 50°C overnight, and pressed into a 1 mm x 19 mm pellet for elemental analysis.

PIXE Analysis

A schematic of the PIXE analysis system at Element Analysis Corporation is shown in Figure 1. A dual energy irradiation is performed on each sample with the X-ray detector in two positions for data collection. During the high-energy (2.1 MeV) irradiation, the detector is in a close-in position with a thick absorber and during the low-energy (1.6 MeV) irradiation, the detector is in a backed-out position with no absorber. Variable charge collection at these two energies/positions allows for spectrum balance and flexibility in the analysis on either the high- or low-energy ends of the X-ray spectrum.

Protons enter the target chamber by passing through a 0.30 mil Kapton window and the X-rays exit through a 0.1 mil Mylar window that is at 45 degrees relative to the beam. The beam, which is at an angle of 23° relative to the sample surface, is swept over the target to irradiate a 16 mm diameter area. The sample chamber is flushed with helium at atmospheric pressure to reduce sample heating and charging and each sample is irradiated for 15 minutes. A typical PIXE spectrum of a coal sample is shown in Figure 2. Data analysis is performed using a modified version of the GUPIX³ PC-based software package. In order that the accuracy and precision of the measurements may be assessed, the results for the PIXE analysis of 7 samples of the NIST 1635a Subbituminous Coal standard reference material are presented in Table 1.

RESULTS & DISCUSSION

In general, HNO_3 was more effective than NaOH in reducing elemental concentrations for all elements except V and Ga. The increase in the concentration of Cu and Cr in certain tests was attributed to corrosion of fittings in the autoclave reactor.

Table 1. Results for NIST SRM 1635a Subbituminous Coal

Element	PIXE Result ^a	Certified Value ^b
Sodium	0.21 ± 0.02 %	(0.24 ± 0.02 %)
Magnesium	760 ± 71 ppm	(1040 ± 130 ppm)
Aluminum	0.30 ± 0.02 %	(0.29 ± 0.03 %)
Silicon	0.60 ± 0.03 %	(0.59 ± 0.05 %)
Sulfur	0.39 ± 0.02 %	0.33 ± 0.03 %
Potassium	113 ± 11 ppm	(96 ± 16 ppm)
Calcium	0.69 ± 0.02 %	(0.54 ± 0.03 %)
Titanium	213 ± 8 ppm	(202 ± 6 ppm)
Chromium	1.2 ± 0.9 ppm	2.5 ± 0.3 ppm
Manganese	19.8 ± 1.2 ppm	21.4 ± 1.5 ppm
Iron	0.23 ± 0.01 %	0.239 ± 0.005 %
Nickel	Below LOD	1.74 ± 0.10 ppm
Copper	3.1 ± 0.2 ppm	3.6 ± 0.3 ppm
Zinc	4.6 ± 0.9 ppm	4.7 ± 0.5 ppm
Selenium	Below LOD	0.9 ± 0.3 ppm
Bromine	1.3 ± 0.3 ppm	(1.4 ± 0.4 ppm)
Strontium	129 ± 9 ppm	(121 ± 19 ppm)

^aAverage and standard deviation of the analysis of 7 samples^bValues in parentheses are the recommended or consensus values

The degree to which elements are removed by coal cleaning processes depends to a great extent on their mode of occurrence or chemical association in the coal. Although the exact composition can vary greatly from one coal to the next, generalizations have been made concerning common modes of occurrence for trace elements in coal.⁴ For example, the fact that Mg, Ca, Mn, and Sr have a carbonate association would explain their efficient removal since the solubilities of carbonates increase in acidic solutions. Moreover, elements known to have an association with pyrite, Fe, S, As, Zn, Ni, and Ga, all show a significant decrease in concentration. Similarly, a considerable reduction in elements known to be strongly associated with silicates, Si, Al, Mg, and K, was observed. Elements thought to have a significant organic association were removed less efficiently by HNO₃. In these samples, those elements were V, Cr, Ti, and Cu. X-ray absorption fine structure spectroscopy of Kentucky #9 coal has indicated a partial organic association for V, Cr, and Ti. Although the association of Cu has not been determined in these samples, Cu is known to have partial organic associations in other coals.

An increase in the duration and pressure of the hydrothermal leaching process showed negligible improvement in the reduction of elemental concentrations for some elements and only slight improvements for others. Thus, it appears these variables have minimal impact on the effectiveness of this coal cleaning process.

SUMMARY

The variable with the greatest impact on hydrothermal leaching appears to be the leaching agent itself. A significant reduction in the concentration of many elements was observed with the use of 2% HNO₃. On the other hand, increasing the reaction time from 15 minutes to 1 hour and/or the vessel pressure from 100 psi to 300 psi had only a slight impact on the removal of hazardous elements in coal.

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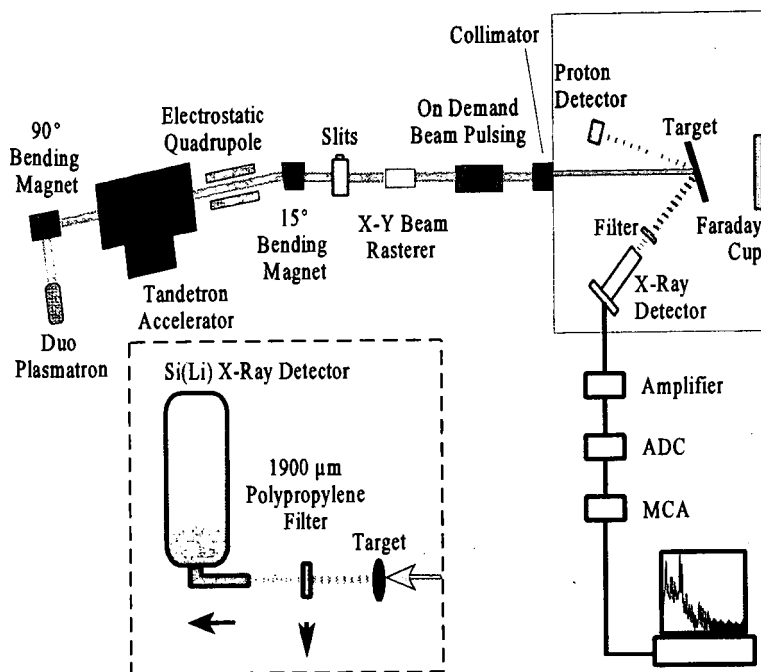


Figure 1. Schematic diagram of PIXE system.

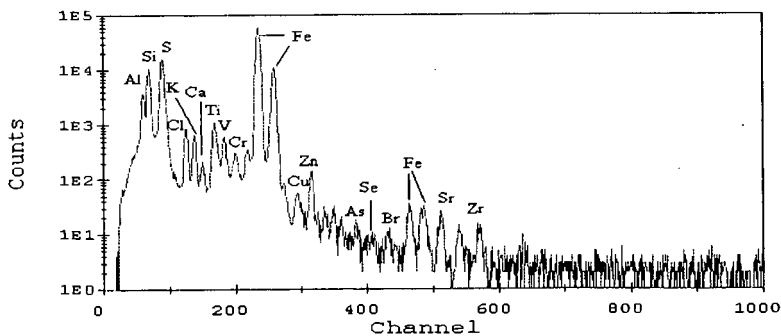


Figure 2. Typical PIXE spectrum of coal.

XANES SPECTROSCOPIC CHARACTERIZATION OF SELECTED ELEMENTS IN DEEP-CLEANED FRACTIONS OF KENTUCKY #9 COAL

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INTRODUCTION

Cleaning of pulverized (-200 mesh) coal is a potentially cost-effective strategy for removing mineral matter and associated minor and trace elements from coal prior to combustion, thereby minimizing the release of pollutants to the atmosphere during combustion. Of special concern are those trace elements designated as potential hazardous air pollutants (HAPs) in the 1990 Amendments to the Clean Air Act¹. Various physical and chemical cleaning methods have been examined with regard to their efficiency for removal of trace elements from coal. Although the mode of occurrence is recognized to be a key factor in determining the behavior of a given element with respect to a specific cleaning method, no study, as far as we are aware, has attempted to include such information.

In this study, a finely ground sample of Kentucky #9 coal from the Illinois coal basin region in western Kentucky has been subjected to a combination of physical cleaning and chemical leaching methods. Each generated fraction has then been characterized using proton-induced X-ray emission (PIXE) spectroscopy to determine the bulk chemical composition and X-ray absorption fine structure (XAFS) spectroscopy to determine information relevant to the elemental mode of occurrence for selected elements. As we will show, inclusion of the mode of occurrence information explains much of the variable efficiency exhibited with respect to the cleaning process by different elements. Conversely, the superior efficiency of column flotation for removal of mineral matter from clean coal provides samples in which the elements exist almost entirely in organic association. Such samples have proven to be invaluable for generating the XAFS spectral signatures for elements in organic association.

EXPERIMENTAL

(a) Coal Cleaning Studies: A 50 kilogram sample of Kentucky #9 coal was made available for this study by the Big Rivers Utility company. The coal, originally consisting of 1" lumps, was dried and crushed to 28 mesh. A representative kilogram sample of the 28 mesh coal was then ground to 80% passing 60 mesh, from which two head samples of 150 grams each were prepared and submitted for analysis. Samples were then prepared for gravity separation testing and release analysis, the results of which are described elsewhere².

A representative sample was then ground to 90% passing 325 mesh to constitute the fine coal sample. Aliquots of this sample were subjected to separation by flotation in a Denver cell and also in a 2"-diameter "Ken-Flote" column³ into float and tailings fractions. The float fraction from the Denver cell was then used as feed for hydrothermal leaching tests that were conducted in a 1 liter autoclave at 110°C and 300 psi. Four samples were prepared: samples were exposed for 15 and 60 minutes to either a 10% acid (H₃PO₄) or basic (NaOH) medium. The overall sample scheme and sample labelling notation are shown in Figure 1. Sufficient samples of each fraction were obtained for proximate analysis, chemical analysis by PIXE spectroscopy, and element speciation analysis by XAFS spectroscopy.

(b) PIXE Spectroscopic Analysis: Each generated sample in the scheme shown in Figure 1 was analyzed by thick-target PIXE spectroscopy using the dual-energy irradiation procedure⁴. NIST coal and fly-ash SRMs were used to monitor the accuracy and precision of the trace element measurements. Results for the SRMs and detection limits for the PIXE measurements are given elsewhere⁴; further details of PIXE analysis can be found in the preceding paper in this volume.

(c) XAFS Spectroscopic Analysis: XAFS spectroscopy of selected elements in the samples generated according to the scheme shown in Figure 1 was carried out either at the National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory, NY, or at the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, CA. Similar experimental procedures were used at both of these facilities; these procedures have been described in detail in previous publications^{5,6}. The XAFS spectra from elements in coal were collected in fluorescence geometry using a thirteen-element germanium detector developed principally for

trace element investigation⁷. Spectra were obtained typically from 100 eV below the K-edge of the element under investigation to as much as 500 eV above the edge. As is usually done, the XAFS spectra were subdivided into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. In many instances, particularly when the concentration of the element was less than about 50 parts-per-million (ppm), the EXAFS signal was too weak to be reliably interpreted and interpretation of the mode of occurrence of an element was based exclusively on the XANES region.

The XANES spectra shown in this paper have been prepared from the raw XAFS spectroscopic data in the usual manner: the spectra are first normalized to the edge step and any slope in the data is removed by fitting spline functions to the pre-edge and post-edge regions and subtracting the pre-edge background extended beneath the overall spectrum. Each spectrum shows a zero-point of energy that is defined by the position of the same absorption edge in a standard material, the spectrum of which is collected at the same time as the spectrum from the coal. For the elements discussed in this paper, these zero points are defined in standard materials as follows: potassium (3608.4 eV, KCl), calcium (4038.1, calcite CaCO₃), titanium (4966 eV, Ti metal foil), vanadium (5465 eV, V metal foil), chromium (5989 eV, Cr in stainless steel), manganese (6539 eV, Mn metal foil), arsenic (11867 eV, As₂O₃). ⁵⁷Fe Mössbauer spectroscopy, rather than Fe XAFS spectroscopy, was used to examine the different forms of iron in some of the fractions shown in Figure 1 because this method is more definitive for elucidating details regarding the iron minerals present in coal.

Table 1: PIXE Analytical Data for Head, Float and Tailings Samples from Denver Cell and "Ken-Flote" Column Flotation Tests

	Sample				
	Head	DC-1	DC-2	CF3-1	CF3-2
Wt fraction, wt%	100.00	72.33	27.67	83.17	16.83
Ash content, wt%	18.29	5.69	50.88	3.56	84.20
Sulfur, wt%	2.96	2.25	5.49	2.94	6.29
Elements in ppm					
Na	5010	2523	--	4233	5852
Mg	5392	2381	10006	3456	20743
Al	19463	8479	57138	11705	103127
Si	45258	15197	129760	17462	222744
S	29095	22446	54905	19432	62873
Cl	3632	1113	--	1529	244
K	4181	1418	10019	1135	15962
Ca	2597	1592	34524	1107	41068
Ti	1249	931	2430	711	2797
V	159	59	187	36	133
Cr	40	31	84	19	98
Mn	37	43	491	21	401
Fe	18173	13465	78278	8612	55967
Ni	21	25	67	19	55
Cu	8	17	47	12	44
Zn	47	20	154	13	108
Ga	7	5	11	3	10
As	10	14	100	10	50
Br	22	26	27	12	12
Sr	41	21	75	15	23

RESULTS AND DISCUSSION

A. Cleaning Efficiency:

Coal characterization data and PIXE analysis data on elemental concentrations are summarized for the different float and tailings fractions in Table 1. The two flotation methods are both efficient at separating the inorganic matter from organic matter, but the column flotation test is definitely the better of the two methods. This is also illustrated in Figure 2, which provides a direct comparison of the two methods. In general, the float/tailings difference indicators in this figure are longer for the column flotation method than for the Denver cell method for most of the elements. It is also instructive to examine the tailings/float concentration ratio for individual elements (or equivalently comparing the length of the indicators in Figure 2) to that for the

overall ash. The elements that exceed or equal the overall ash ratio are Ca and Mn; those that are slightly less than the overall ash ratio are Al, Si, K, and Zn in both tests, and Fe along with As in the case of the Denver cell test. Not surprisingly, sulfur shows a small value for the ratio because over 40% of the element is organically bound. However, there is a group of elements consisting of Ti, V, Cr, Ni, Ga, that also have relatively short indicators, suggesting that significant fractions of these elements might also be in organic association.

Attempts to mass balance individual elements in these flotation experiments vary from good to poor and certainly the differences for a number of elements are much larger than can be attributed to experimental errors in the PIXE analysis. The most significant problem would appear to be segregation of the heavy minerals (pyrite, calcite) in the feed sample as the largest variations between the flotation experiments are exhibited by calcium, manganese and iron. In particular, the calculated feed composition for the column flotation experiment has significantly lesser amounts of these elements and somewhat more Al and Si (derived from excess clays?) than that for the Denver cell flotation test.

B. The Lithophile Elements:

XANES spectra of Ti, V, Cr, and Mn showed quite different spectra for the float and tailings fractions (e.g. for Mn, Figure 3). Whereas the XANES spectra of the tailings fractions could be attributed to principally (>80%) illite for Ti, V and Cr, and to a mixed mineralogical occurrence for Mn (25% Mn/illite and 75% Mn/calcite), the spectra of the float fractions did not match the spectra of any mineral standard examined and distinct organically associated forms were inferred to exist for these four elements. For Ti and Cr, the closest matches appeared to be a poorly crystalline oxide or oxyhydroxide, a possibility raised in earlier studies⁹ of V in Kentucky #9 coal. For Mn, the spectrum of the float fraction was altered significantly by application of both the base and acid leaching tests and the Mn content was also reduced in both tests. This suggested the presence of two organically associated forms of Mn: one that was soluble in acid; the other soluble in base.

Examination of the XANES spectra of calcium, a major element, also showed distinctly different spectra for the tailings and float fractions. The spectra of the tailings fractions were clearly dominated by Ca as calcite, whereas the spectra of the float fractions were similar to that observed for carboxyl-bound Ca in low-rank coals⁹. Interestingly, K XANES spectra of all fractions, whether float or tailings, were identical to that of K in illite. The fact that illitic Ti, V, and Cr spectra were only seen for the tailings fraction and not for the float fraction suggests that there are two generations of illite in the coal: one generation is coarse and/or easily separated from the coal (e.g. partings) and contains all of the minor elements; the other generation is fine, can not be separated easily from the organic matter, and is essentially devoid of significant Ti, V, and Cr. These two illite forms might represent coarse detrital and fine-grained authigenic generations of illite in the coal, respectively.

C. The Chalcophile Elements:

In contrast to the lithophile elements, the two chalcophile elements examined, Fe and As, were found in the same forms in both the tailings and float fractions. Both Fe and As are found in association with pyrite and its oxidation products in all fractions. Arsenic occurs as a substitutional replacement for sulfur in the pyrite structure and as arsenate. The arsenate form is more prevalent in the float fractions (Figure 4), consistent with the fact that smaller particle sizes of pyrite are both more likely to be found in the float fractions and to be more oxidized than large particle sized pyrite. The Mössbauer data for iron tells a very similar story. Iron in oxidized form (principally jarosite) is relatively more common compared to iron as pyrite in the float fractions than in the tailings fractions. There is an approximate linear correlation between the fraction of oxidized arsenic and the fraction of Fe as jarosite for all the samples examined. This relationship would imply perhaps that the arsenate is incorporated in the jarosite structure, presumably by substitution of the arsenate group for the sulfate group in the jarosite structure.

CONCLUSIONS

The results of this study demonstrate convincingly that Ca, Ti, V, Cr and Mn in Kentucky #9 coal occur in both a mineralogical and an organic association. For Ti, V, and Cr the mineralogical association consists principally of substitution in the cation layers in the clay mineral illite, whereas Mn substitutes mainly for Ca in calcite, which is the major mineral occurrence for calcium. The organic association has not been so clearly identified, but is consistent with the elements present in oxygen coordination, either at individual isolated ion-exchange sites on maceral surfaces, or in microparticles of poorly crystalline oxide or oxyhydroxide minerals. For Ti, V, and Cr, this organic association represents approximately 50% of the occurrence of these elements in this particular sample of Kentucky #9 coal. In contrast to the five lithophile elements, the chalcophile elements, Fe and As, appear to occur almost

exclusively in pyrite or its oxidation products in all fractions of this coal. Such occurrences readily explain the relatively poor separation of some of these elements (Ti, V, Cr) in flotation tests.

Finally, this investigation demonstrates that information on elemental modes of occurrence from XAFS spectroscopy is a very useful supplement for the interpretation and understanding of results from coal cleaning studies. Conversely, the mineral-rich and mineral-poor fractions generated in the course of such studies provide the means for a much better understanding of elemental occurrences based on XAFS spectroscopy. This serendipitous relationship will be exploited for investigation of other coals and cleaning processes.

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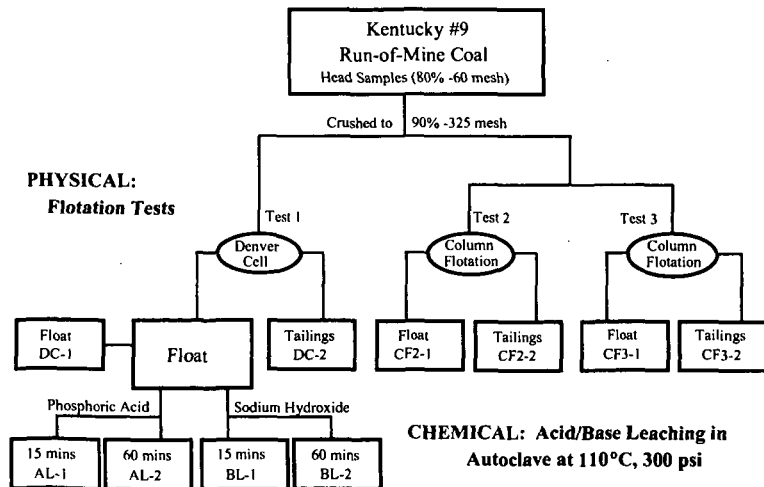


Figure 1: Scheme for physical and cleaning tests performed on the as-mined sample of Kentucky #9 coal to generate float, tailings, and leached fractions.

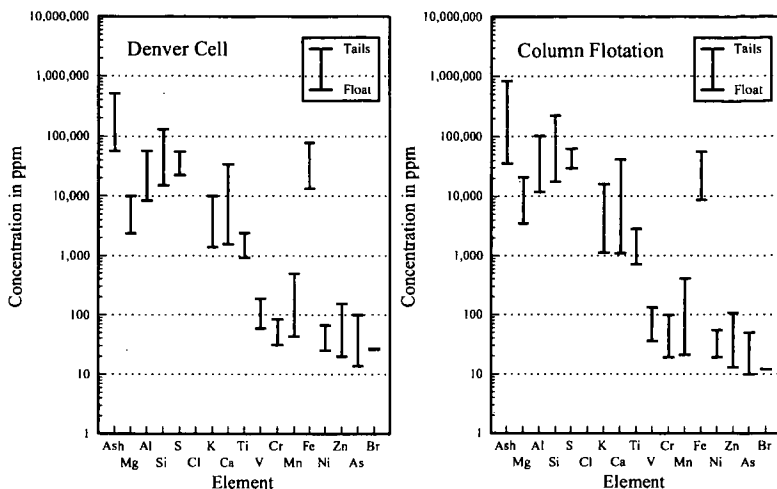


Figure 2: Comparison of the relative efficiency of the segregation of elements in Kentucky #9 coal between float and tails fractions generated in the Denver cell test and in the "Ken-Flote" column flotation test.

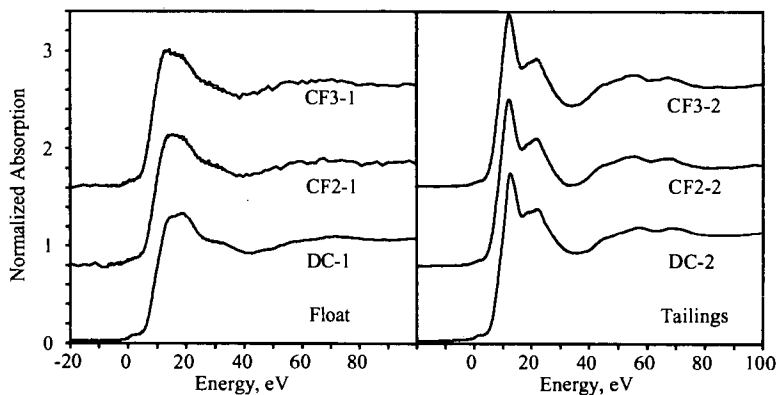


Figure 3: Mn XANES spectra of float and tails fractions of Kentucky #9 coal.

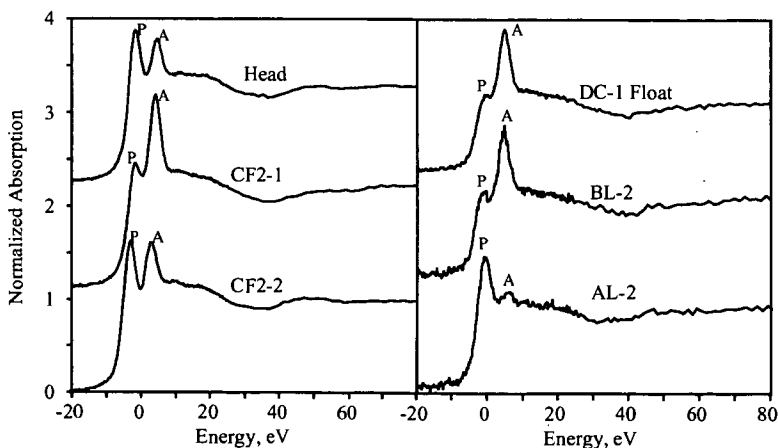


Figure 4: As XANES spectra of various fractions of Kentucky #9 coal.

WASHABILITY OF AIR TOXICS IN MARKETED ILLINOIS COALS

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INTRODUCTION AND BACKGROUND

The 1990 Clean Air Act Amendments (CAA) require that the health risks resulting from the atmospheric emissions of 189 hazardous air pollutants (HAPs) from various industrial sources be assessed and, if needed, emission limits be established [U.S. Public Law 101-549, 1990]. Of these 189 HAPs, 16 elements (As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb, Se, Th, U) occur in coal in trace or minor quantities, and may be emitted into the atmosphere during combustion. Electrical utilities are presently exempt from compliance with the CAA requirements for HAPs. This may, however, change after the U.S. Environmental Protection Agency (EPA) completes its risk analyses and promulgates emission standards as prescribed by law.

The U.S. Geological Survey (USGS) has a substantial amount of data on HAPs in channel samples of coals from various regions of the U.S. The U.S. EPA will use this database for its risk assessment of HAPs emissions from coal-fired power plants. Because Illinois coals shipped to utilities are cleaned at conventional preparation plants, and conventional cleaning decreases levels of most HAPs in marketed Illinois coals relative to channel samples [Demir et al., 1994a], the USGS data on channel samples would overestimate the emission of HAPs from combustion of these coals at utilities.

Recent reviews of the environmental aspects of trace and minor elements in coal [Swaine, 1989; Clarke and Sloss, 1992; Wesnor, 1993] indicated that (1) modern pollution control systems can trap up to more than 90% of fly ash generated during coal combustion and (2) trace elements that "escape" during combustion are either emitted in gas phase or attached to ultrafine fly ash particles that are not captured by the pollution control systems. Highly volatile HAP elements (Hg, Cl, F) are mostly or partially volatilized in the flue gas, while less volatile ones (As, Cd, Pb, P, Sb) generally vaporize, oxidize, and then, upon cooling, condense onto the fly ash particles (Fig. 1). The least volatile HAPs (Mn, Th) are enriched in bottom ash and slag. Other HAPs (Se, Be, Co, Cr, Ni, U) exhibit mixed behavior depending on their mode of occurrence in the feed coal, the characteristics of coal and mineral matter, and types and operational conditions of combustion units.

Coal cleaning is an attractive alternative to costly post-combustion control of air toxics emissions from power plants. Reviews that summarized progress in the removal of trace and minor elements, including HAPs, via coal cleaning include Mezey [1977], National Research Council [1979, 1980], Wheelock and Markuszewski [1981, 1984], Streeter [1986], Kaiser Engineers [1989], Jacobsen et al. [1992], and Norton et al. [1986, 1989, 1992]. These reviews show that physical coal cleaning can be economical and effective for significantly decreasing the content of most HAPs prior to combustion. In general, physical cleaning becomes efficient if a high degree of comminution is utilized to free mineral matter from the macerals. Those elements associated (either physically disseminated or bonded chemically) with the macerals are not easily removed; in some cases, their concentrations may actually be enhanced in the cleaned coal. Recent studies [Paul and Honaker, 1994; Honaker and Reed 1994] indicated that mineral matter content of finely ground Illinois Basin coals can be effectively decreased using advanced gravity separators.

It has been generally recognized that the cleaning efficiency of gravity separators for fine-sized coal cannot be estimated from conventional, static float-sink (F-S) tests. Centrifugal F-S procedures, however, could successfully predict the cleanability of -28-mesh (<0.589-mm) size coal [Harrison, 1986; Franzidis and Harris, 1986; Cavallaro and Killmeyer, 1988; Ho and Warchol, 1988; Bosold and Glessner, 1988; Dumm and Hogg, 1988; Suardini, 1993].

The purpose of this study was to generate F-S washability data to estimate how much more the HAP content of marketed Illinois coals can be decreased if advanced gravity-based coal cleaning was used at coal preparation plants. Washability data for twelve HAP elements (As, Be, Co, Cr, Mn, Ni, P, Pb, Sb, Se, Th, U) in 27 coal samples ground to -100 mesh (<149 μ m) and in 8 coal samples ground to -200 mesh (<74 μ m) are reported and discussed.

EXPERIMENTAL

Samples and Sample Preparation

Each of the 27 samples of marketed coals was collected from a different coal preparation plant in Illinois. The samples are from five different regions of Illinois coal field (Fig. 2), and are preserved under nitrogen at the Illinois State Geological Survey (ISGS). Collection, preparation, and storage of the samples were described by Demir et al. [1994a,b].

Representative splits of the 27 samples were dry-ground in a hammer mill so that 90% of the particles were smaller than 100 mesh (149 μ m). Also, eight of the 27 samples were wet-ground in a rod mill (700 grams coal + 700 mL tap water) generally for 30 minutes so that 90% of the particles were smaller than 200 mesh (74 μ m). The coal slurry from the rod mill was filtered and air-dried. The -100 and -200 mesh samples were saved under nitrogen for the subsequent washability tests.

Washability Tests

A centrifugal float-sink (F-S) method based on the methods reported in Ho and Warchol [1988] and Cavallaro and Killmeyer [1988] was used to determine the washabilities of both ash and HAPs. The washability test procedure was as follows:

- (1) Mix about 100-g of coal sample dried at 40°C overnight with 2 L of coalgrav[®] liquid (mixture of tetrachloroethylene and naphtha) with a specific gravity (s.g.) of 1.3 to generate a slurry containing about 5% coal. Add dispersing reagent (Aerosol OT) to the mixture to achieve a dosage of about 5 mg reagent per g of coal.
- (2) Agitate the mixture with a mechanical stirrer for 6 to 10 minutes and then in an ultrasonic bath until no agglomeration persists (usually 2 to 10 minutes).
- (3) Pour the slurry into 250-mL Teflon centrifuge bottles, tightly cap the bottles, and place the bottles in a centrifuge.
- (4) Centrifuge the slurry at 2000 rpm (about 880 g force for the centrifuge used) for 20 minutes.
- (5) Gently stir the float portion of the slurry in the bottles without disturbing the sink portion. Centrifuge the slurry again at 2000 rpm for 20 minutes.
- (6) Repeat step 5.
- (7) Gently pour the float out of the bottles onto a filter paper placed in a filter funnel. The pouring of the float portion usually does not significantly disturb the sink portion which becomes tightly compacted during the 1-hour centrifugation.
- (8) Filter the float and then wash it thoroughly, first with 250 mL of ethanol, and then 1.5 L of deionized water, to remove residues of coalgrav[®] and dispersing agent. Dry the float overnight at 40°C and weigh it.
- (9) Mix the sink from step 8 with 2 L of 1.4 s.g. coalgrav[®], and repeat steps 2 through 8. A small amount of lower s.g. liquid trapped in the wet sink during the preceding step does not measurably alter the s.g. of the new suspension.
- (10) Mix the sink from step 9 with 2 L of 1.6 s.g. coalgrav[®], and repeat steps 2 through 8.
- (11) Wash, dry, and weigh the sink as in step 8.
- (12) Submit the <1.3, 1.3-1.4, 1.4-1.6, and >1.6 s.g. F-S fractions for chemical analysis.

Chemical Analysis and Preparation of Cleaned Composite Samples

The 27 samples of marketed coals were analyzed for the 12 HAPs and ash and all of their F-S fractions were analyzed for ash using well-established procedures for common coal analyses at the ISGS (Table 1). The combustible materials content of each F-S fraction was calculated by subtracting its ash and moisture contents from 100. Then a plot of %cumulative combustibles recovery vs cumulative weight of F-S fractions was constructed for each F-S test. Using these plots, the first two or three lightest fractions from each test were successively combined so that the composite sample contained 80% of the combustible materials in the parent coal. All 80%-combustibles recovery products were analyzed for the 12 HAPs and ash.

RESULTS AND DISCUSSION

The analytical data for the feed coals and their clean washability products (Table 2) were used to estimate the ability to remove HAP elements from finely-ground marketed Illinois coals through the use of advanced gravity separators. The ranges of average concentrations for 12 HAP elements in the 27 samples of marketed Illinois coals (Fig. 3) were as follows:

<2 mg/kg:	Be, Sb, Se, Th
2-10 mg/kg:	As, Co, U
10-20 mg/kg:	Cr, Ni, Pb
>20 mg/kg:	Mn, P

The concentrations of all HAPs, except Be, in the coals were decreased (with a few exceptions) as a result of F-S separation at -100 mesh size (Table 3, Fig. 4). Some of the decreases (or enrichments) of element concentrations calculated for some individual samples may be erroneous if the difference between the concentration of a given element in the parent coal and that in its clean F-S product is not greater than the analytical precision for that particular element. Such decrease and enrichment errors, however, generally cancel each other when mean values for the entire sample set are computed. On average, Be was enriched in the -100 mesh washability products by 94% when compared with the parent coals. This suggests that Be was finely disseminated (perhaps organically associated) within the coal macerals. Because some of Be tends to stay with bottom ash and slag during coal combustion (Fig. 1), and because the mean concentration of Be in the marketed coals was only 1.3 mg/kg (Fig. 3), additional environmental risk due to an average of 94% enrichment of this element could be very small.

The decrease in ash content ranged from 37% to 75% with an average of 53% (Table 3, Fig. 4). As a result, 9 of the 27 clean F-S products had ash contents of 2.77% to 3.86% (Table 2). The average decreases for As, Mn, and P exceeded that for ash, indicating that these three elements were somewhat enriched in relatively coarse mineral grains that were effectively removed during the F-S process; As was likely associated mainly with pyrite, Mn with calcite, and P with apatite. Precombustion removal of As from coal is important because of its relatively high atmospheric mobility during coal combustion (Fig. 1). The decrease of Se, another element with relatively

high atmospheric mobility (Fig. 1), was smaller than that of As but still significant (37%). The average decreases for Cr(20%), Sb(19%), and U(11%) were relatively small. Although Sb can be mobilized by attachment to air-borne fly ash particles, its small concentrations (Table 2, Fig. 3) could limit any environmental risk associated with Sb emission from combustion of marketed Illinois coals. Atmospheric emissions of Cr and U are expected to be small because they tend to be fixed in coarse ash and slag during coal combustion.

Grinding the 8 coals to -200 mesh (<74 μm) resulted in greater average decreases for Sb, Se, and Th and a smaller decrease for Mn when compared with decreases obtained for -100 mesh (<149 μm) samples of the same coals (Table 4, Fig. 5). The changes in the amount of decrease of other elements and ash for -200 mesh samples relative to -100 mesh samples were not significant. It should be noted that additional tests with varying centrifuge speed and amount and type of dispersant should be conducted to determine whether the F-S separation efficiency for -200 mesh samples can be increased.

The marketed coal products are currently ground to 70% passing 200 mesh (74 μm) size for utilization in pulverized coal boilers which comprise over 90% of the combustion units used in Illinois [Honaker et al., 1994]. Therefore, because there would be no extra cost for grinding, an advanced coal cleaning strategy that would substantially decrease HAPs, as well as ash and sulfur, in Illinois coals beyond conventional cleaning can be economical. Furthermore, as much as 10% of the production of many coal preparation plants in Illinois is fine coal waste. An efficient and low cost cleaning of this fine coal waste would generate additional clean coal and thus increase revenues from mined coal. Using clean coal would not only reduce atmospheric HAPs emissions but also slagging and fouling at coal-fired power plants.

SUMMARY AND CONCLUSIONS

Float-sink washability data on 27 samples of marketed Illinois coals indicated that, at -100 mesh (<149 μm) particle size and with an 80%-combustibles recovery, the ash contents of the coals can potentially be decreased by 37% to 75% with an average of 53%, beyond conventional cleaning, using advanced gravity-based coal cleaning. As a result, some of the clean products could have ash contents of less than 3%. Decreases in ash contents were accompanied by decreases in the levels of eleven HAPs (As, Co, Cr, Mn, Ni, P, Pb, Sb, Se, Th, U) investigated, with a few exceptions. The average decreases for As, Mn, and P exceeded that for ash. The average decrease of Se was smaller than that of ash but still significant (37%). Precombustion removal of As and Se from coal is important because of their relatively high atmospheric mobility during coal combustion. On average, Se was enriched in the washability products by 94% compared with the parent coals. Because of its low concentrations in the coals and its low atmospheric mobility, the enrichment of Se caused by fine coal cleaning could increase any related environmental risk only slightly. The average decreases for Cr(20%), Sb(19%), and U(11%) were relatively small. Although Sb can be enriched in air-borne fly ash particles, any environmental risk associated with atmospheric Sb emission could be small because marketed Illinois coals generally have Sb concentration of about 1 mg/kg or less. Most of Cr and U are expected to be fixed in coarse ash and slag rather than emitted into the atmosphere during coal combustion. The grinding of 8 of the coals to -200 mesh (<74 μm) increased the removal of Sb, Se, and Th, decreased that of Mn and did not significantly change those of other HAPs compared with the -100 mesh (<149 μm) samples of the same coals. An efficient and low-cost fine coal cleaning of marketed Illinois coals could reduce not only the atmospheric HAPs emissions but also slagging and fouling at coal-fired power plants.

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Table 1. Relative precision and detection limits of methods commonly used for analyses of HAPs and ash in coal samples

Element	Relative precision %	Average detection limit	Methods*				
			WDXRF	AAS	INAA	OEP	PyroIC
Major and minor oxides (%)							
MnO	ash 5	0.01	X				
P ₂ O ₅	ash 5	0.02	X				
Trace elements (mg/kg)							
As	coal 7	1.0			X		
Be	ash 5	0.5				X	
Cd	ash 10	2.5		X			
Co	coal 5	0.3			X		
Cr	ash 2	7.0			X		
F	coal 10	20.0					X
Hg	coal 15	0.01		X**			
Ni	ash 10	15.0		X	X		
Pb	ash 20	25.0		X		X	
Sb	coal 10	0.2			X		
Se	coal 10	2.0			X		
Th	coal 5	0.4			X		
U	coal 15	3.0			X		

Constituent	Absolute precision (%)		Accuracy (%)		ASTM method (1992)		
Ash	0.10		0.5		D5142-90		

* WDXRF = wavelength-dispersive x-ray fluorescence spectrometry

AAS = atomic absorption spectrometry

INAA = instrumental neutron activation analysis

OEP = optical emission (photographic) spectrometry

PyroIC = pyrohydrolysis and ion chromatography

** Hg by cold vapor atomic absorption spectrometry

Table 2. Chemical composition of samples of marketed Illinois coals (feed) and their clean F-S fractions at 80% combustibles recovery (product). Ash values are in wt% and elemental values are in mg/kg (all values are on a dry basis). One-half the detection limit was used, for those values less than the detection limit, in the computations of means and standard deviations.*

FEED COAL NO.	MESH REGION SIZE	As	Asn	Co	Cr	Mn	Ni	P	Pb	Sb	Se	Th	U
		coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.	coal prod.
C32773	1 -100	8.72	5.01	1.3	9.1	1.0	2.3	2.0	4.1	22	42	22	1.2
C32774	1 -100	7.07	2.77	1.0	3.1	1.0	3.1	0.9	5.8	12	11	10	1.2
C32777	1 -100	14.52	7.87	5.1	1.2	1.2	2.2	1.5	1.6	11	4	87	1.2
C32782	1 -100	9.8	4.79	1.0	2.9	2.2	4.8	4.6	3.8	12	9.4	38	1.1
C32785	1 -100	11.62	5.89	2.4	0.9	<1.0	2.2	1.6	1.2	14	9.7	55	1.1
C32785	1 -100	9.75	4.38	2.3	0.7	1.1	2	3.1	2.5	15	7	7	1.1
C32797	1 -100	10.29	5.99	4	1.1	2	3.1	2.5	1.5	12	18	11	1.1
C32814	1 -100	9.6	3.86	6.4	2.6	4	3.1	2.5	1.5	12	18	11	1.1
C32814	1 -100	9.6	3.86	6.4	2.6	4	3.1	2.5	1.5	12	18	11	1.1
C32798	2 -100	10.52	4.32	2.2	0.8	1.1	2.3	2.8	2.1	12	12	12	1.1
C32798	2 -100	13.16	7.23	2.2	0.8	1.1	2.3	2.8	2.1	12	12	12	1.1
C32800	2 -100	13.39	7.23	2.2	0.8	1.1	2.3	2.8	2.1	12	12	12	1.1
C32813	2 -100	14.7	7.88	2.4	1.0	1.4	1.4	3.5	2.1	42	22	40	1.1
C32815	2 -100	12.03	5.01	3	0.9	<1.0	2.1	2.7	1.7	14	11	61	1.1
C32784	3 -100	8.13	3.32	18	9.3	1.8	3.5	4.2	2.5	11	8.9	17	1.1
C32795	3 -100	5.76	2.79	3.6	2.2	1	1.0	4.8	4.6	8.6	7.0	11	1.1
C32799	3 -100	11.42	3.48	17	1.6	4.4	4.0	12	8.6	64	5.0	15	1.1
C32803	3 -100	8.18	3.11	10	1.6	2.7	2.1	12	9.1	28	9.0	14	1.1
C32803	3 -100	9.19	5.25	4.1	1.8	2.7	2.1	12	9.1	28	9.0	14	1.1
C32665	4H -100	9.39	3.8	4.4	1.3	1.2	1.0	3.6	2.1	13	12	25	1.1
C32771	4H -100	12.57	4.29	3.7	0.9	1.1	1.6	4.1	1.9	14	12	35	1.1
C32776	4H -100	9.27	4.16	2.7	1.0	1.5	1.4	3.6	2.3	15	13	38	1.1
C32862	4S -100	7	3.67	14	5.2	1.4	2.7	4.4	2.8	10	7.8	15	1.1
C32772	4S -100	9.33	4.34	8	2.6	1.1	1.0	3.9	2.3	9.2	8.2	39	1.1
C32781	4S -100	9.71	5.19	4.3	1.4	4.0	1.1	2.7	1.7	12	9.9	37	1.1
C32793	4S -100	14.14	3.59	30	8.4	1.2	2.0	5.5	3.7	13	7.0	39	1.1
mean	all	10.06	4.69	7.1	2.4	1.3	2.4	3.4	2.3	14	11	41	1.1
stdev	all	2.37	1.35	7.3	2.5	0.8	2.1	1.0	0.9	6.7	3.4	35	1.1
C32773	1 -200	8.72	4.87	1.3	0.6	1	1.6	2.3	1.8	12	10	38	1.1
C32774	1 -200	7.07	2.65	1.0	0.4	1	1.6	2.3	1.8	12	10	38	1.1
C32794	2 -200	10.52	5.69	2.3	1.0	1.1	2.1	2.8	1.8	12	7.9	40	1.1
C32813	2 -200	14.7	5.67	2.4	0.8	1.4	2.7	3.5	2.3	42	21	40	1.1
C32784	3 -200	8.13	3.21	18	6.0	1.8	2.4	4.2	2.8	11	9.0	17	1.1
C32865	4H -200	9.39	3.47	4	0.9	1.2	1.9	3.6	2.3	13	12	25	1.1
C32771	4H -200	12.57	5.17	3.7	1.0	1.1	1.8	4.1	2.8	14	34	36	1.1
C32772	4S -200	9.33	3.62	8	1.7	1	1.4	3.9	2.8	9.2	9.1	39	1.1
mean	all	10.05	4.29	7.5	2.4	1.6	2.9	3.4	2.3	15	11	32	1.1
stdev	all	2.33	1.12	6.9	2.5	0.9	2.4	0.6	0.5	10.5	4.3	9	1.1

* blank spaces indicate that no data were available at the time of this writing

Table 3. Percent changes in ash and HAPs contents as a result of F-S separation of 27 samples of marketed Illinois coals ground to -100 mesh. Each clean F-S product contained 80% of the combustible materials of its parent sample. Negative values indicate decreases and positive values enrichments. In the statistical computations, one-half the detection limit was used for all values below the detection limit.*

FEED COAL	NO.	REGION	Ash	As	Be	Co	Cr	Mn	Ni	P	Pb	Sb	Se	Th	U
C32773	1	-43	-62	0	-13	-8	-67	-9	-50	-17	0	-37	-17	-71	
C32774	1	-61	-55	175	-71	-24	-72	-73	-40		-33	-25	-25	25	
C32777	1	-46	-76	-83	7	-9	-83	-14	-61	-39	-27	-31	-18	-36	
C32778	1	-51	-71	118	-17	-22	-68	-19	-55	-36	0	-33	-20	44	
C32782	1	-49	-63	340	-25	-31	-73	0	-70	-17	-20	-47	-18	8	
C32785	1	-55	-70		-31	-29	-69	-39	-76		-50	-51	-23	-22	
C32797	1	-46	-73		-23	-15	-63	-13	-64	0	-29	-27	-5		
C32814	1	-44	-59	55	-40	9	-77	-17	-57	-39	-21	-15	0	-15	
C32779	2	-60	-53	360	-35	-24	-69	-45	-61	-14	-25	-48	-31	0	
C32794	2	-59	-65	109	-25	0	-73	-43	-61	-33	-33	-42	-21	-10	
C32798	2	-54	-64	120	-42	-39	-70	-6	-60	-79	0	-59	-24	-4	
C32800	2	-37	-50		-18	-26	-53	-44	-60	0	-46	-25	-21		
C32813	2	-46	-58	0	-40	-48	-60	-38	-64	-46	-29	-46	-29	-24	
C32815	2	-58	-70	320	-37	-21	-70	-40	-70	-79	-33	-52	-29	0	
C32784	3	-59	-48	94	-40	-19	-62	-40	-30		-9	-21	-36	-50	
C32795	3	-52	-39	0	-4	-19	-64	-22	-30	-38	0	-27	-33	-58	
C32799	3	-70	-91		-9	-28	-92	-13	-37		-17	-31	-44	0	
C32801	3	-44	-54		-32	-17	-57	-50	-30		0	-27	-27	0	
C32803	3	-43	-56		-22	-8	-64	-46	-61		-25	-40	-19	18	
C32661	4H	-51	-56	56	-54	-19	-65	-64	-61	-37	-40	-50	-33	-16	
C32665	4H	-60	-70	-17	-42	-8	-76	-55	-70	-68	-25	-47	-31	-2	
C32771	4H	-66	-76	45	-54	-14	-78	-10	-61	-41	-33	-43	-39	-5	
C32776	4H	-55	-63	-7	-36	-13	-74	-42	-61	30	-14	-29	-36	6	
C32662	4S	-48	-63	93	-36	-22	-60	-29	-58	-52	-20	-31	-37	-16	
C32772	4S	-53	-68	0	-41	-11	-79	-31	-49	-15	-14	-23	-23	0	
C32781	4S	-47	-67	120	-37	-17	-73	-18	-70	-30	-29	-48	-25	-25	
C32793	4S	-75	-75	67	-33	-46	-79	-32	-67	-69	-8	-18	-56	-25	
mean all		-53	-64	94	-31	-20	-70	-32	-57	-38	-19	-37	-28	-11	
stdev all		9	10	117	16	12	8	18	13	25	14	12	10	24	

* blank spaces indicate that no data were available at the time of this writing.

Table 4. Percent changes in ash and HAPs contents as a result of F-S separation of 8 samples of marketed Illinois coals ground to -100 and -200 mesh. Each clean F-S product contained 80% of the combustible materials of its parent sample. Negative values indicate decreases and positive values enrichments. In the statistical computations, one-half the detection limit was used for all values less than the detection limit.*

FEED COAL	MESH															
NO.	REGION	SIZE	Ash	As	Be	Co	Cr	Mn	Ni	P	Pb	Sb	Se	Th	U	
C32773	1	-100	-43	-62	0	-13	-8	-67	-9	-50	-17	0	-37	-17	-71	
C32774	1	-100	-61	-55	175	-71	-24	-72	-73	-40		-33	-25	-25	25	
C32794	2	-100	-59	-65	109	-25	0	-73	-43	-61	-33	-33	-42	-21	-10	
C32813	2	-100	-46	-58	0	-40	-48	-60	-38	-64	-46	-29	-46	-29	-24	
C32784	3	-100	-59	-48	94	-40	-19	-62	-40	-30		-9	-21	-36	-50	
C32665	4H	-100	-60	-70	-17	-42	-8	-76	-55	-70	-68	-25	-47	-31	-2	
C32771	4H	-100	-66	-76	45	-54	-14	-78	-10	-61	-41	-33	-43	-39	-5	
C32772	4S	-100	-53	-68	0	-41	-11	-79	-31	-49	-15	-14	-23	-23	0	
mean	all		-56	-63	51	-41	-17	-71	-37	-53	-37	-22	-36	-28	-17	
stdev	all		7	8	64	16	14	7	20	13	18	12	10	7	29	
C32773	1	-200	-44	-54	60	-22	-17	-38	-27	-41	-17	-50	-53	-25	-71	
C32774	1	-200	-63	-63	125	-55	12	-72	-60	-40		-25	-58	-25	25	
C32794	2	-200	-46	-57	91	-36	-34	-53	-57	-41	83	-33	-53	-36	-20	
C32813	2	-200	-61	-67	93	-34	-50	-58	-50	-69	-81	-14	-70	-43	-14	
C32784	3	-200	-61	-67	33	-33	-18	-47	-40	-20	-20	-18	-43	-43	0	
C32665	4H	-200	-63	-80	58	-36	-8	-56	-18	-61	-68	-50	-53	-38	-7	
C32771	4H	-200	-59	-73	64	-32	0	-44	10	-50	-68	-33	-50	-33	-5	
C32772	4S	-200	-61	-79	40	-28	-1	-62	-31	-55	-59	-14	-46	-31	0	
mean	all		-57	-68	71	-35	-15	-54	-34	-47	-33	-30	-53	-34	-12	
stdev	all		7	9	29	9	19	10	22	14	53	14	8	7	26	

* blank spaces indicate that no data were available at the time of this writing.

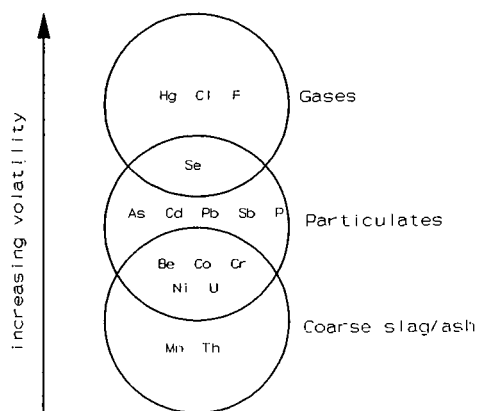


Figure 1. Enrichment of HAPs in different coal combustion and gasification products (after Clarke and Sloss, 1992).

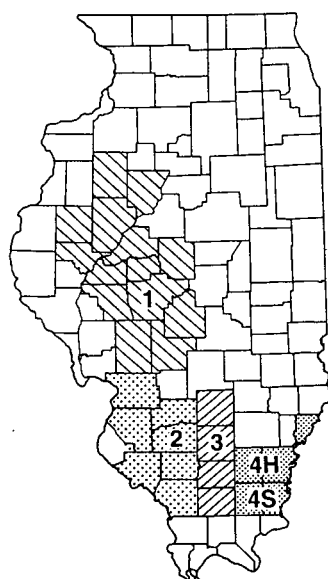


Figure 2. Sample regions of Illinois coal field. Region 4 was subdivided by seam into Herrin (H) and Springfield (S) coals.

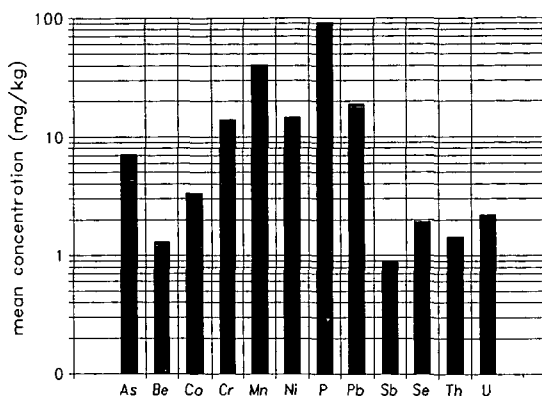


Figure 3. Mean concentrations of 12 HAPs in 27 samples of marketed Illinois coals.

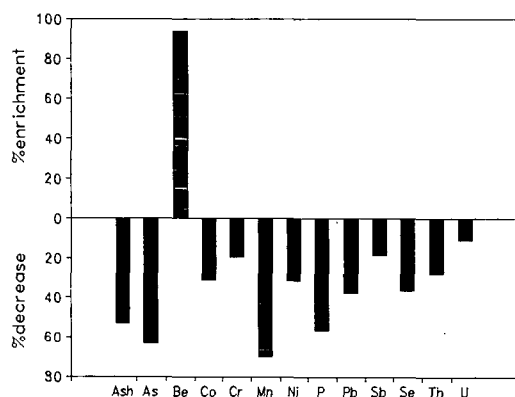


Figure 4. Average estimated changes in concentrations of 12 HAPs in 27 samples of marketed Illinois coals ground to -100 mesh if an advanced gravity separation process were applied and 80% of the combustible materials recovered from the process.

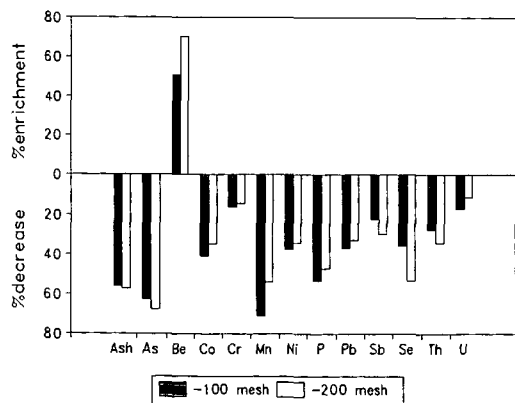


Figure 5. Average estimated changes in concentrations of 12 HAPs in 8 samples of marketed Illinois coals ground to -100 and -200 mesh if an advanced gravity separation process were applied and 80% of the combustible materials recovered from the process.

TRACE ELEMENT CONTENT OF CLEANED ILLINOIS BASIN COAL

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Keywords: Trace metals, coal, scanning electron microscopy

ABSTRACT

Illinois Basin coal samples treated to extract organic sulfur and selected hazardous air pollutants (HAPs) were examined for trace metal content using scanning electron microscopy with wavelength-dispersive spectrometry (SEM-WDS). The extraction process used subcritical water, defined as water held in the liquid state under sufficient pressure to remain liquid at temperatures greater than the normal boiling point, but below the supercritical point of water (218 atm and 374°C). The samples were sink-floated to remove pyrite prior to receiving the subcritical extraction treatment. Some mineral matter remains in the coal, including sulfates, aluminosilicates, and small amounts of pyrite. In individual mineral grains in the unextracted coal, mercury is found intermittently at levels up to 0.62 wt%, arsenic at up to 0.28 wt%, and selenium at up to 0.38 wt%. These occurrences appear to be localized concentrations.

INTRODUCTION

Scanning electron microscopy with wavelength-dispersive spectrometry (SEM-WDS) is useful for determining the trace metal content of materials in situations where high spatial resolution is desired. The technique is more time-consuming than atomic absorption or other methods used to determine bulk trace element content of materials, but the additional effort required provides information unobtainable through other means. For coal samples, use of SEM-WDS allows the associations of trace metals with particular minerals in coal to be determined. This approach is particularly important in gaining the information necessary to determine how coal-cleaning processes work.

METHODS

Samples were mounted in carnauba wax, cross-sectioned, polished, and carbon-coated to improve conductivity. Analyses were conducted on a JEOL 35C scanning electron microscope equipped with two JEOL wavelength-dispersive spectrometers with xenon-filter proportional counters and a Noran Instruments energy-dispersive spectrometer. The microscope is controlled by a Noran Instruments Voyager 2 computer system.

The microscope was operated at an accelerating voltage of 25 kV with a beam current of 100 nA. Wavelength-dispersive spectral peaks were counted for 100 s. Live time for each energy-dispersive spectrum used to obtain major-element chemistry was 30 s. Certified standards were used for calibration. The data were subjected to ZAF (atomic number, absorption, and fluorescence) corrections following collection. The detection limit for arsenic, selenium, and mercury using the SEM-WDS technique is approximately 0.01 wt%.

Four samples of Illinois Basin Coal were characterized: raw IBC-101, extracted IBC-101, raw IBC-102, and extracted IBC-102. The extracted coals were treated with subcritical water, defined as water held in the liquid state under sufficient pressure to remain liquid at temperatures greater than the normal boiling point, but below the supercritical point of water (218 atm and 374°C). The samples were sink-floated to remove pyrite prior to receiving the subcritical extraction treatment. Arsenic, selenium, and mercury were measured in individual mineral grains from each raw and extracted coal. Major element composition was also determined.

RESULTS AND DISCUSSION

Results show that trace metals are distributed irregularly throughout the mineral matter in the four samples. Data are presented in Tables 1 through 4 for the IBC-101 raw coal, IBC-101 extracted coal, IBC-102 raw coal, and IBC-102 extracted coal, respectively. The mineral grains analyzed represent a wide variety of compositions, including aluminosilicate, calcium sulfate, pyrite, and iron oxide. The copper-rich grains analyzed represent an additive used in the extraction process.

The most dramatic difference in major element composition between raw and extracted coal samples is for sulfur. Sulfur is abundant in both of the raw coal samples, but is almost entirely absent in the extracted samples, demonstrating that the extraction process is effective at removing this element. Iron is present at high levels in both raw and extracted samples.

Arsenic, selenium, and mercury occur in both raw and extracted samples, suggesting that the coal-cleaning process may not completely remove these trace metals. In the IBC-101 samples, mercury and selenium appear to have been reduced by the extraction process, but arsenic is more abundant in the extracted sample. In the case of the IBC-102 sample, the extraction process may have added mercury, as this element is present in a greater proportion of the mineral grains and in higher concentrations in the extracted sample than in the raw sample. Arsenic and selenium occur with roughly equivalent frequency and concentration in the raw and extracted IBC-102 samples. Most of the mineral grains analyzed contained one or more of these elements, although none of the grains contained all three of the trace metals measured.

CONCLUSIONS

Results presented here show that the distribution of trace metals in raw and extracted coals varies greatly. Arsenic, selenium, and mercury were found to be associated with a range of mineral compositions and are present even in low-pyrite cleaned coals. The extraction process appears to remove sulfur effectively, but some trace metals may remain in the coal after treatment.

TABLE 1

Elemental Composition of Individual Mineral Grains in IBC-101 Raw Coal										
Point No.	Trace Metals, wt%			Major Elements, wt%						Total, wt%
	As	Se	Hg	Al	Si	P	S	Ca	Fe	
1	ND*	0.02	0.37	ND	ND	ND	36.11	ND	63.49	99.99
2	ND	0.38	0.13	ND	ND	ND	43.04	56.46	ND	100.01
3a	ND	0.01	0.04	ND	ND	2.12	40.05	57.79	ND	100.01
3b	ND	0.04	ND	ND	ND	ND	39.97	48.17	11.83	100.01
3c	ND	0.03	0.62	ND	ND	ND	42.24	57.12	ND	100.01
3d	ND	0.02	ND	ND	13.23	ND	40.92	45.83	ND	100.00
3e	0.02	0.01	ND	2.99	9.75	ND	34.51	34.01	18.71	100.00
3f	ND	0.03	ND	ND	ND	ND	44.34	55.64	ND	100.01
3g	ND	0.01	ND	ND	10.19	ND	32.72	17.58	39.51	100.01
3h	0.28	0.02	ND	8.73	28.70	ND	15.74	ND	44.35	100.00
3i	ND	0.01	ND	ND	ND	ND	44.03	55.97	ND	100.01
3j	ND	0.02	ND	6.41	20.19	ND	11.58	5.60	56.21	99.99
3k	0.01	0.02	ND	ND	ND	ND	12.43	ND	87.54	100.00
4a	ND	ND	ND	ND	ND	ND	20.25	ND	79.74	99.99
4b	ND	ND	ND	ND	ND	ND	20.43	ND	79.58	100.01
4c	0.01	ND	ND	ND	ND	ND	21.30	ND	78.68	99.99
4d	0.07	0.01	ND	7.73	14.45	ND	36.96	ND	40.77	99.99
4e	ND	ND	ND	17.01	21.42	ND	24.78	ND	36.80	100.01
4f	0.01	0.01	ND	35.45	64.53	ND	ND	ND	ND	100.00
4g	0.01	0.01	ND	ND	ND	ND	41.66	ND	58.33	100.01
4h	0.01	0.01	ND	34.62	65.37	ND	ND	ND	ND	100.01

* Not detected.

TABLE 2

Elemental Composition of Individual Mineral Grains in IBC-101 Extracted Coal											
Point No.	Trace Metals, wt%				Major Elements, wt%						Total, wt%
	As	Se	Hg	Mg	Al	Si	S	Ca	Ti	Fe	
1	ND*	0.01	ND	ND	27.23	12.07	ND	ND	ND	60.68	99.99
2	ND	ND	ND	ND	49.95	50.05	ND	ND	ND	ND	100.00
3	ND	0.01	ND	ND	ND	ND	ND	ND	ND	99.99	100.00
4	ND	ND	ND	ND	56.84	43.16	ND	ND	ND	ND	100.00
5	0.03	0.02	ND	ND	ND	4.78	ND	ND	ND	ND	100.00
6	ND	0.03	ND	ND	ND	ND	ND	ND	ND	99.97	100.00
7	ND	ND	ND	ND	ND	ND	ND	ND	ND	100.00	100.00
8a	0.06	ND	ND	7.66	ND	26.11	ND	23.02	ND	43.15	100.00
8b	0.14	ND	ND	3.78	ND	7.21	ND	24.47	ND	64.39	99.99
8c	0.12	ND	ND	9.42	ND	32.32	ND	12.19	6.10	39.85	100.00
8d	0.25	ND	ND	23.42	ND	51.39	ND	ND	ND	24.94	100.00
8e	0.07	ND	ND	2.70	ND	26.98	ND	49.81	8.83	11.62	100.01
8f	0.18	ND	ND	10.33	ND	24.13	ND	7.29	2.74	55.33	100.00

* Not detected.

TABLE 3

Elemental Composition of Individual Mineral Grains in IBC-102 Raw Coal											
Point No.	Trace Metals, wt%			Major Elements, wt%							Total, wt%
	As	Se	Hg	Al	Si	S	Ca	Ti	Fe	Zn	
1	ND*	0.03	ND	ND	ND	34.00	ND	ND	ND	65.96	99.99
2	ND	0.01	ND	ND	ND	37.94	ND	ND	62.05	ND	100.00
3	0.01	ND	ND	ND	ND	50.91	ND	ND	49.08	ND	99.99
4	ND	ND	ND	ND	ND	52.79	ND	ND	47.21	ND	100.00
5	ND	0.01	ND	ND	ND	46.74	ND	ND	53.25	ND	100.00
6	ND	ND	ND	ND	ND	50.66	ND	ND	49.33	ND	99.99
7	ND	ND	ND	ND	3.53	40.75	55.72	ND	ND	ND	100.00
8	ND	ND	ND	ND	ND	52.84	ND	ND	47.16	ND	100.00
9	ND	ND	ND	ND	0.93	55.84	ND	ND	43.23	ND	100.00
10	0.01	ND	ND	5.79	4.24	48.05	ND	ND	41.91	ND	100.00
11	0.02	ND	0.01	ND	ND	55.25	ND	ND	44.72	ND	100.00
12	ND	ND	ND	ND	ND	ND	100.00	ND	ND	ND	100.00
13	ND	ND	0.01	24.62	51.98	ND	ND	2.90	9.55	ND	100.01
14	0.03	ND	0.01	ND	ND	53.30	ND	ND	46.66	ND	100.00
15	0.01	ND	ND	16.69	40.93	19.90	ND	ND	12.62	ND	100.01
16	ND	ND	ND	ND	ND	53.25	ND	ND	46.75	ND	100.00
17	ND	ND	ND	ND	ND	54.71	ND	ND	45.29	ND	100.00

* Not detected.

TABLE 4

Elemental Composition of Individual Mineral Grains in IBC-102 Extracted Coal										
Point No.	Trace Metals, wt%			Major Elements, wt%						Total, wt%
	As	Se	Hg	Al	Si	S	Mn	Fe	Cu	
1	0.01	0.01	ND*	ND	ND	ND	ND	99.98	ND	100.00
2	0.02	0.03	ND	ND	ND	ND	ND	99.94	ND	99.99
3	0.03	0.03	ND	ND	ND	ND	ND	99.93	ND	99.99
4	0.06	0.05	ND	ND	ND	ND	ND	99.89	ND	100.00
5	ND	ND	ND	ND	ND	ND	ND	ND	100.00	100.00
6	ND	ND	0.08	ND	ND	ND	ND	99.92	ND	100.00
7	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00
8	ND	ND	0.02	ND	ND	ND	ND	99.98	ND	100.00
9	ND	ND	ND	ND	ND	ND	ND	2.47	97.52	99.99
10	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00
11	ND	ND	ND	ND	ND	ND	ND	100.00	ND	100.00
12	ND	ND	0.08	ND	0.48	ND	0.60	98.84	ND	100.00
13	0.03	ND	0.06	ND	ND	0.52	ND	99.38	ND	99.99
14	ND	ND	0.05	ND	ND	ND	ND	99.95	ND	100.00
15	ND	ND	0.06	ND	ND	ND	ND	99.93	ND	100.00
16	ND	ND	ND	ND	ND	ND	ND	100.00	ND	100.00
17	ND	ND	0.05	ND	ND	ND	ND	99.95	ND	100.00
18	ND	ND	0.02	ND	ND	ND	ND	99.98	ND	100.00
19	ND	ND	0.03	ND	ND	ND	ND	99.97	ND	100.00
20	ND	ND	0.04	ND	ND	ND	ND	99.96	ND	100.00
21	ND	ND	0.01	ND	ND	ND	ND	99.99	ND	100.00

* Not detected.

CHROMIUM VALENCE FORMS OF COAL FLY ASH IN THE SOLID STATE AND LEACHATES

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Keywords: Cr speciation, solution chemistry of Cr in leachates, carbon paste electrode

INTRODUCTION. Speciation of chromium in fly ash is a significant and complicated issue. Huggins et al. [1] used a synchrotron X-ray method to show that most of the chromium in coal fly ash is Cr(III), an important finding that should be evaluated further. Also, questions pertaining to the bioavailability of Cr and its phase distribution in fly ash, whose determination is subject to the redox chemistry of fly ash, will need to be answered for risk assessment purpose.

METHODOLOGY. Cr(VI) in leachates was determined by cathodic stripping voltammetry (CSV), and Cr(III), Cr(total) as Cr(VI) after H_2O_2 treatment [2,3]. Independent analysis of Cr(III) and Cr(VI) was achieved by either separating Cr(III,VI) on Chelex 100 [4] prior to CSV or by using a diphenylcarbazide (DPCI)-modified carbon paste electrode (CPE) in cyclic voltammetry of the mixture [5]. By doping CPE with fly ash and/or standard and using it in a DPCI-containing electrolyte, the Cr valence forms in the solid state were quantitated. Fe(II,III) speciation was carried out spectrophotometrically [6]. The Tessler procedure modified for phase separation and digestion of Ni in fly ash [7] was adapted for Cr speciation. SRM 1633b was obtained from NIST and CFF ash samples from Dr. Huggins of the Univ. of Kentucky.

RESULTS AND DISCUSSION. Table 1 shows Cr(VI) to be 72-82% of total Cr in the 50% HF digest of 4 coal fly ash samples, contradicting the X-ray solid analysis by Huggins et al. [1]. The SRM ash was extracted sequentially and compared with total digestion for valence form and mass balance. As shown in Table 2, the water-soluble and bioavailable Cr (Step 1) is only Cr(III). No Cr was detected in the iron oxide matrix (Step 2). The electromagnetic Cr phase (Step 3) may be Ni-Cr alloy or CrO_2 . In acid extractions, Cr(III) was 1.8 times of Cr(VI) in HCl, but Cr(VI) was 2.6 times of Cr(III) in HF. The summation of Cr(III) in extracts 1-5 was 41% vs. 27% in the total digest. Starting with the residue of Step 3 where the water-soluble, iron oxide, and magnetic phases were removed, Table 3 showed that the 2-step acid extraction yielded 35% of total remaining Cr as Cr(III) vs. 29% from the single step treatment. In all these extractions, the Cr mass balance was 99-100%. It seems likely that redox chemistry in different leachates may have effected these varying ratios of Cr valence forms.

To understand redox chemistry in Cr speciation, the Fe(II,III) species in the 5 sequential extracts of 1633b are shown in Table 4. The absence of Fe(II) in leachate 1 is indicative of the true origin of Cr(III) identified therein. Table 5 validates the reducing power of Fe(II) and FeS_2 in 3 extractants. For comparison, arsenite did not reduce Cr(VI) at pH 5 but gave partial reduction in acid (cf. Table 6). In leachates 4 and 5, there was no Fe(II) detected and Cr(VI) was observed. In Table 6 is shown the partial oxidation of Cr(III) by MnO_2 at pH5 and complete oxidation in acid. The latter may be responsible for generating Cr(VI) in the acid leachates of the coal fly ash.

Solid state voltammetric peaks of Cr(III) at 600 mV (Fig. 1A) and Cr(VI) at -600 mV (Fig. 1B) are diagnostic of Cr valence forms. Direct Cr speciation of 2 coal fly ash, Fig. 2 for SRM 1633b and Fig. 3 for LS102, revealed Cr(III) only, whose oxidation peak was enhanced by spiking with Cr_2O_3 (Fig. 4,5). The quantitation of Cr(III) shown in Table 7 agrees to within 5% of the total Cr found in the HF-digested samples. In Fig. 6 is shown the emergence of the Cr(VI) peak at -600 mV in the residue of 1633b heated in 2N HCl for 2 h, which disappeared after heating it for 4 h. A similar phenomenon is seen in Fig. 7 for 1633b heated in 50% HF but the Cr peaks were broadened due to more extensive leaching. The Cr species in the solids and leachates of 1633b were determined to obtain closure. As shown in Table 8, Cr(III) in 1633b was either oxidized to Cr(VI) and detectable on the residue surface or dissolved and then partly oxidized in solution.

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Table 1. Voltammetric analysis of chromium valence states of HF digests of coal fly ash

Samples ^a	Cr(VI) ug/g	Cr Total ug/g	Cr(VI) Cr Total
			%Total
CFF-LS100	116.3	155.1	75.0
CFF-LS102	112.1	137.4	81.6
CFF-LS100/FLT	108.8	140.8	77.3
SRM 1633b	142.0	196.4	72.3

^a CFF samples were obtained from Dr. F.E. Huggins, Univ. of Kentucky, who showed Cr(III) to be the predominant species by XAFS spectroscopy.

Table 2. Chromium speciation of SRM 1633b by phase separation

Sequential Extraction	Cr(III)		Cr(VI)		Cr(ttl)	
	ug/g	%	ug/g	%	ug/g	% certified ^a
1. NaOAc, pH5	13.0	100.0	0.0	0.0	12.7	6.7
2. Na2S2O4-Citrate pH5	0.0	0.0	0.0	0.0	0.0	0.0
3. Electromagnet	-	-	-	-	5.9	3.0
4. 2N HCl, heat	30.2	64.9	16.4	35.1	46.8	24.0
5. 50% HF, heat	35.6	28.1	91.1	71.9	129.4	66.4
Extracts 1 to 5	78.8	41.0	107.5	59.0	194.8	100.1
50% HF (total digest)	53.5	26.9	145.4	73.1	196.4	99.1

^a Cr certified 198.2 ug/g

Table 3. Comparison of chromium valence state of SRM 1633b by 2 extractions

A: Electromagnet residue ----- 2N HCl ----- 50% HF

B: Electromagnet residue ----- 50% HF

Sequential Extractions	A			B		
	Cr(III) ug / g	Cr(VI) ug / g	Cr(Tot) ug / g	Cr(III) ug / g	Cr(VI) ug / g	Cr(Tot) ug / g
2N HCl	30.7	16.5	46.6			
CV%	4.0	3.1	2.6			
50% HF	30.9	97.7	127.8	50.3	123.8	175.3
CV%	4.8	2.9	2.3	3.0	2.8	4.6
Subtotal	61.6	114.2	174.4	50.3	123.8	175.3
% Valence	35.0	65.0		28.9	71.1	

Table 4. Mass balance of Fe determination in 5-step extraction of SRM 1633b

Extraction step	Fe2+ found (ug/g)	Fe3+ found (ug/g)	Fe(T) found (ug/g)	% Certified
1. NaOAc, pH 5	0.0	2076.8	2076.8	2.7
2. Na2S2O4-citrate, pH 5	6367.0	0.0	6367.0	8.2
3. electromagnet	5447.7	9990.2	15437.9	19.9
4. 2 N HCl, heat	0.0	8144.4	8144.4	10.5
5. 50 % HF, heat	0.0	45462.6	45462.6	58.7
Total	11814.7	65674.0	77488.7	100.0

Fe Certified in 1633b: 77800 ug/g

Table 5. Fate of Cr(VI) in the presence of Fe(II) and FeS2 in extractions

Extractant	A, Cr Recovered		B, Cr Recovered			
	Cr(III)		Cr(III)		Cr(VI)	
	ug	%	ug	%	ug	%
NaOAc, pH5 Bransonic	4.72	94.4	0.00	0.0	0.96	96.0
2N HCl, heat	4.91	98.2	0.96	96.0	0.00	0.0
50% HF, heat	4.88	97.6	1.05	105.0	0.00	0.0

A: 5 ug Cr(VI) + 50 ug Fe(II)

B: 1 ug Cr(VI) + 10 mg FeS2

Table 6. Fate of Cr(III) and Cr(VI) in the presence of arsenite and MnO2

Extractant	A, Cr Recovered				B, Cr Recovered			
	Cr(III)		Cr(VI)		Cr(III)		Cr(VI)	
	ug	%	ug	%	ug	%	ug	%
NaOAc, pH5 Bransonic	0	0	4.77	95.4	2.30	46.0	2.80	56.0
2N HCl, heat	2.35	4.7	2.47	49.4	0.00	0.0	4.76	95.2
50% HF, heat	2.31	46.2	2.44	48.8	0.00	0.0	4.80	96.0

A: 5 ug Cr(VI) + 5 ug As(III)

B: 5 ug Cr(III) + 10 mg As(V)

Table 7. Solid state Cr speciation of fly ash by CPE^a

Fly Ash	Peak Current uA	Cr(III) found ug/g	CV %	Cr(total) ^b ug/g
SRM 1633b ^c	8.46	205.5	2.5	195
CFF-LS102	5.60	135.4	4.9	137

^a Carbon paste electrode: fly ash-CPE in electrolyte: 0.002M H₂SO₄+0.5M KNO₃+10⁻⁴M DPCI; single peak from anodic scan, no Cr(VI) peak in cathodic scan; CV from 3 separate analysis

^b Cr determined after digestion of fly ash in 50% HF

^c Certified Cr 198.2 ug/g

Table 8. Chromium sepeciation of SRM 1633b in solids and leachates

Treatment	Cr in solids ^a (ug/g)		Cr in leachates ^b (ug/g)		Cr(sum) Cr certified %
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
(None) before extraction	205.5	0	0	0	105.4
2N HCl, heat 2h	146.1	9.65	29.4	11.5	99.1
2N HCl, heat 4h	135.4	0	39.4	22.7	99.5
50% HF, heat 4h	0	0	53.9	149.2	102.2

^a 100 mg 1633b--1 g carbon as CPE in electrolyte 0.002M H₂SO₄+0.5M KNO₃+10⁻⁴M DPCI

^b DPCI--MCPE in electrolyte 0.002M H₂SO₄+0.5M KNO₃

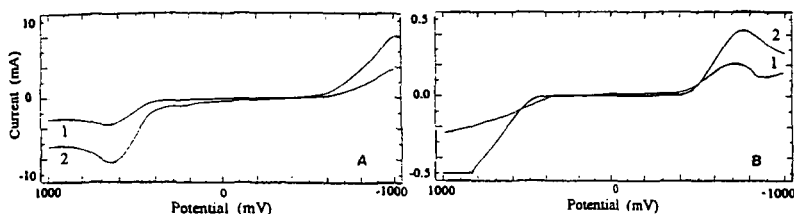


Fig. 1A Oxidation voltammograms of Cr(III) in carbon paste electrode in electrolyte: 2X10⁻³ M H₂SO₄+0.5 M KNO₃+10⁻⁴ M DPCI
1-- 100 mg KCr(SO₄)₂/g carbon
2-- 100 mg Cr₂O₃/g carbon

Fig. 1B Reduction voltammograms of Cr(VI) in carbon paste electrode in the above electrolyte.
1-- 100 mg PbCrO₄/g carbon
2-- 100 mg BaCrO₄/g carbon

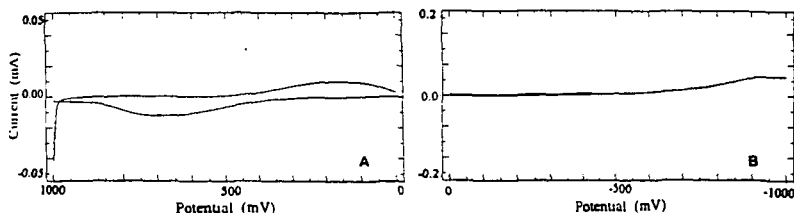


Fig. 2 Cyclic voltammograms of SRM 1633b in carbon paste electrode (100 mg/g) in the above electrolyte,
A--plotted 1000 mV--0 mV at $\pm 50 \mu A$ B--plotted -1000 mV--0 mV at $\pm 200 \mu A$.

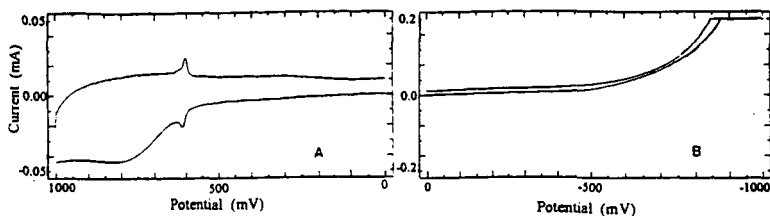


Fig. 3 Cyclic voltammograms of CFF-LS102 in carbon paste electrode (100 mg/g) in the above electrolyte, A—plotted 1000 mV–0 mV at $\pm 50 \mu\text{A}$ B—plotted -1000 mV–0 mV at $\pm 200 \mu\text{A}$.

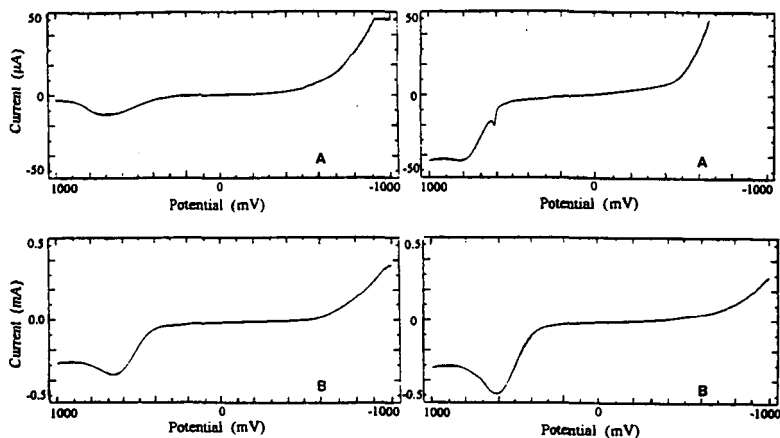


Fig. 4 Oxidation voltammograms of SRM 1633b spiked with Cr_2O_3 in carbon paste electrode in the above electrolyte
A—100 mg 1633b/g carbon
B—0.5 mg Cr_2O_3 added

Fig. 5 Oxidation voltammograms of CFF-LS102 spiked with Cr_2O_3 in carbon paste electrode in the above electrolyte
A—100 mg CFF-LS102 /g carbon
B—0.5 mg Cr_2O_3 added

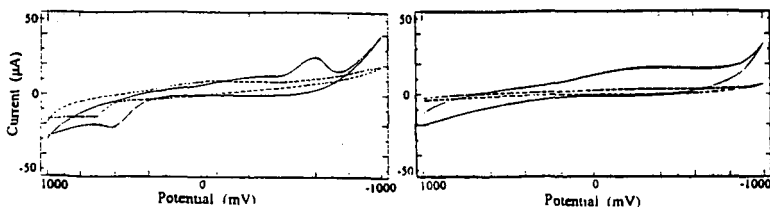


Fig. 6 Cyclic voltammograms of SRM 1633b residue of 2N HCl treatment in carbon paste electrode in the above electrolyte
(—)—140°C, 2 h.
(---)—140°C, 4 h.

Fig. 7 Cyclic voltammograms of SRM 1633b residue of 50% HF treatment in carbon paste electrode in the above electrolyte
(—)—140°C, 2 h.
(---)—140°C, 4 h.

A FUNDAMENTAL INVESTIGATION OF TOXIC SUBSTANCES FROM COAL COMBUSTION

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INTRODUCTION

The Clean Air Act Amendments of 1990 identify a number of hazardous air pollutants (HAPs) as candidates for regulation. Should regulations be imposed on HAP emissions from coal-fired power plants, a sound understanding of the fundamental principles controlling the formation and partitioning of toxic species during coal combustion will be needed. For this reason PSI Technologies, under the support of the U.S. DOE, the Electric Power Research Institute (EPRI), and the Technical Research of Finland (VTT), has teamed with researchers from the USGS and several leading universities to determine the dominant mechanisms that control trace element partitioning in combustion systems. The final objective of this program will be to develop a broadly applicable emissions model useful to regulators and utility planners.

This paper describes the need for this type of fundamentally based emissions model, and some of the important data required to develop such a model. Some of these data include the elemental modes of occurrence in coal of important trace elements, and how these modes of occurrence may control the partitioning of these elements in combustion systems. The current program to study these issues is presented, as are the results obtained to date. Four coals have been selected for their diversity in mineralogy and trace element composition. After a description of the rationale for the approach, preliminary data on coal composition and on modes of occurrence of trace elements in the coals are presented.

RATIONALE

Current understanding about toxic species transformations and partitioning in coal-fired combustion systems points to gaps in data that need to be filled in order to produce a model that will be useful for both new and existing combustion sources. The large amount of data accumulated from field and laboratory tests has defined the general behavior of toxic and trace species during coal combustion. One of the major efforts to collect field data is the Power Plant Integrated Systems Chemical Emissions Study (PISCES) led by EPRI. Within PISCES, EPRI performed an extensive literature search on the partitioning of toxic and trace species into the various output streams of power plants. Detailed field measurements were also made of the concentrations of 22 species in the effluent streams of power plants.¹ This effort has resulted in a large database of emissions of trace and toxic species.² Organic toxins may also be emitted from coal-fired systems. Field studies suggested that emissions of organic species from coal-fired plants are tied to the combustion efficiency and are typically much lower than emissions of inorganic species.³⁻⁵

There appears to be a consensus of opinion that the four most critical trace elements for coal combustion are Hg, As, Cr, and Se. Ni, Mn, and Pb are of lesser concern, while the remaining elements (Sb, Be, Co, Cd) appear to present little cause for concern for coal utilization because of their low abundance in coal and their insignificant contribution to pollution of the atmosphere in comparison to non-coal source.⁶ Chlorine and the other halogens are also of concern. Chlorine, in particular, can be found at concentrations in excess of 1000 ppm in some bituminous coals. Thus for some power plants, either HCl or Cl₂ may exceed the 10 ton/y CAAA limit. Also chlorine may play a key role in determining the volatility of mercury.⁷

Messerole and Chow⁸, using PISCES data, found that several elements, including As, Cd, Hg, and Se, typically vaporize in utility boilers. Some of these condense on flyash particles and are removed by pollution control devices. Others such as Hg, F, and Cl are emitted predominantly as vapors. However, significant variations in trace element behavior were noted, possibly caused by interactions with other minerals or differences in modes of occurrence in the parent coal. This was emphasized by Meij⁷, who observed large differences in Hg and As partitioning as coal type was varied in one utility boiler unit. These differences were attributable to differences in the mode of occurrence and the combustion transformations of these metals. If the fundamental mechanisms that govern the behavior of these species were understood, the utility industry could better predict emission rates.

This need increases in importance when unique fuels, equipment configurations, and operating conditions are considered.

Other investigators have studied the behavior of trace elements in laboratory combustion systems as reviewed in recent papers.^{10,12} Despite these efforts, mechanistic information is generally lacking. For example, Linak and Wendi¹¹ presented the results from several laboratory and field studies on the enrichment of trace elements in the submicron ash. Although the data set is not entirely consistent for all species, it does show enrichment of several elements in the submicron ash which is most likely to escape from particulate control devices. These elements include Sb, As, Cd, Cr, Pb, Hg, Ni, and Se. Other elements such as Cl were found to remain in the vapor phase.

Previous mineral matter transformation work has demonstrated the critical importance of the *forms* or *modes* of occurrence of trace elements in coal on their behavior during combustion.^{12,13} The mode of occurrence of an element is important because of the tremendous diversity in which an element can be found in coal.^{14,15} An element can be completely dispersed throughout the coal macerals or can exist within its own discrete mineral phase. Organically associated metals such as sodium typically vaporize during combustion. Metals contained in clays, on the other hand, typically do not vaporize. Bool and Helble showed that the volatility of a number of trace metals is dependent on elemental form in the coal.¹² Quann et al. noted the importance of form in a systematic study of twenty different coals burned under well-characterized conditions.¹⁷

One of the first methods developed for estimating emissions from power plants was the use of empirical emissions factors.^{10,18} For example, based on data from five boilers, Brooks reports an average emission factor of 684 lb/10¹² Btu for arsenic in uncontrolled dry-bottom pulverized coal boilers.¹⁰ Although emissions factors are useful for preliminary calculations, they are clearly inappropriate for use in determining regulatory compliance or in predicting the effect of fuel and boiler modifications on partitioning and emissions. A more complex model to predict trace species partitioning, based on the PISCES database, has been developed by Rubin and co-workers.^{18,19} This model uses a probabilistic analysis to predict the partitioning of a given element into the various output streams of a coal-fired utility boiler. Boiler configuration inputs are combined with trace element partitioning data from the PISCES database. The model predicts a range of emission values based on the uncertainties of the inputs (i.e., species concentrations in the coal). The model has been shown to predict emissions of several species for specific power plants with a reasonable degree of accuracy.²⁰ Use of the model is best suited to well-defined configurations for which partitioning data are available. Since the PISCES project covered less than 5% of the approximately 1,750 utility boilers in the U.S., many existing facilities fall "outside" the data base. For novel fuels and boiler configurations, the uncertainty in predicted toxic species emission will be high.

The large amount of data accumulated from the field and from laboratory tests has defined the general behavior of toxic and trace species during coal combustion. Concentrations of toxic elements have been measured for many coals. A broad variation in elemental form has been reported for many elements with major data gaps existing. Very little information on the interactions of trace species with major coal minerals is available. The four most critical trace toxic metals that are emitted to the environment by coal combustion are Hg, As, Cr, and Se. Halogens, particularly Cl, are also of key importance. In order to meet the challenges of cleaner power production in the future, a new method is needed to predict emissions of toxic species from a wide range of fuels (and blends) and from many different kinds of combustion systems. The specific approach taken by the team is described below.

TECHNICAL APPROACH

The discussion in the preceding section illustrates the need to perform a comprehensive program to determine how the form of occurrence of an element in coal and the combustion conditions control the partitioning of that element in combustion system. This information, if obtained as part of carefully planned combustion experimentation, will be crucial to better understand the partitioning data collected in full scale units, and to develop a model applicable to all types of coal fired combustion systems. With this objective, the PSIT-led team has begun a multi-year program to determine the forms of occurrence in coal, and the effect of the combustion (and post combustion) environment on partitioning of these elements. Participants in the program include researchers from MIT, Princeton University, University of Arizona, University of Connecticut, University of Kentucky, USGS, and VTT. The following section describes many of the tools that will be used, and the combustion facilities that will be used, to address these issues.

Direct identification of the modes of occurrence of trace inorganic species in coal and ash using unique analytical techniques such as XAFS analysis and selective leaching forms a cornerstone of the approach. Elemental modes of occurrence will be established for the key elements using a combined microscopic/spectroscopic approach. XAFS spectroscopy is currently capable of

supplying information in the middle of the periodic table (Ti-Sn) with abundances in excess of 5 to 10 ppm.¹⁹ Whereas XAFS spectroscopy will provide a specific signature of all modes of a given element in the coal in a single spectrum, the microscopic-based methods will provide valuable complementary information on the spatial distribution and association of the element. This combined approach, which has not been attempted before, should provide the more information than has been available previously about an element's mode of occurrence in coal. Elemental modes of occurrence will also be determined for trace species using an analytical procedure developed by USGS. This protocol combines low temperature ashing, chemical analysis, x-ray diffraction, coal segregation via flotation, leaching, electron microbeam measurements, and low and moderate temperature heating tests to elucidate forms of elements in coal.

Combustion testing will be used to determine the importance of each of four fundamental processes that may influence the speciation and partitioning of trace metals during combustion. These processes are (1) vaporization of metallic species, (2) gas-phase transformations of metallic species, (3) condensation of gaseous metallic species, and (4) solid transformations of metallic species. In general all four of these processes can take place simultaneously and in competition with each other.

A unique aspect of the program is an attempt to isolate and study these steps as much as possible while retaining the conditions that are typically present during coal combustion. *Fundamental bench scale studies* will be used to isolate vaporization and condensation of trace metals. Combustion of size and density-classified coal particles will allow a mechanistic interpretation of vaporization. Thermogravimetric studies of metal vapor-solid interactions will provide information on the interactions between gaseous species and ash particles post-combustion. *Integrated combustion experiments* using utility grind coal samples and realistic combustion stoichiometries will allow the evaluation of excluded mineral and combustion effects. *Self-sustained combustion experiments* using a 100,000 Btu/h coal-fired combustor with realistic heating and cooling rates permits the examination of trace metal partitioning when all the important mechanisms are combined.

A critical review of available field data provides guidance for the overall program direction and model validation. An analysis of steady state and transient organic emissions from field data will be conducted to determine whether organic toxic emissions pose a concern and should therefore be included in ToPEM. Inorganic emissions reported from recent comprehensive field sampling campaigns will also be reviewed and one or more sets of model validation data will be selected from DoE or EPRI field studies consisting of coal composition, combustion conditions, and concentrations of trace metals in solid and gaseous streams, including the effects of back end conditions on trace metal partitioning. The effect of coal type and combustion conditions on submicron ash morphology will also be assessed using data collected by VTT.

COAL CHARACTERIZATION

Four coals have been acquired for the Phase I baseline studies. All coals are currently being used by utilities in the United States and represent a diversity of coal and mineral types. The coals are (1) Illinois 6 (Burning Star No. 4 mine), (2) Washed Pittsburgh Seam (Blacksville mine), (3) Eastern Kentucky coal (Elkhorn and Hazard seams), and (4) Wyodak subbituminous (Black Thunder mine). All coals will be analyzed for trace element content (Instrumental Neutron Activation Analysis), for iron oxidation state (Mössbauer spectroscopy), mineral distribution (Computer Controlled Scanning Electron Microscopy), and for forms of trace elements (XAFS and selective leaching).

Preliminary work on the mode of occurrence of arsenic in two bituminous coals, Pittsburgh and Elkhorn/Hazard, has been completed. The form of occurrence of As in coal may have an effect on the vaporization behavior during combustion. Most As in U.S. coals is associated with the sulfide phase (i.e., pyrite).²¹ Oxidation of the pyrite in coal will result in the formation of arsenates. Preliminary evidence suggests that arsenic associated with pyrite may volatilize more readily than arsenates.²²

Mössbauer spectroscopy was used to assess the oxidation state of iron in the Pittsburgh and Elkhorn/Hazard coals. Virtually all the iron in the Pittsburgh coal is present as pyrite, whereas almost one-third of the iron in the Elkhorn/Hazard coal is present in other forms (clays, siderite, and jarosite). The presence of jarosite may be an indication of oxidation of pyrite in the coal. The Elkhorn/Hazard coal showed 12% of the iron as jarosite, while for the Pittsburgh coal only 2% jarosite was detected.

Based on a previous XAFS study of arsenic occurrence in U.S. bituminous coals,²² three forms of As have been identified in these coals. Arsenical pyrite, in which As substitutes for Fe in FeS₂, is the most common. Arsenate compounds (AsO₄³⁻) are the next most common and arsenopyrite (FeAsS) is the least common. Oxidation of arsenical pyrite has been shown to produce arsenate compounds. In the present work XANES spectroscopy for As was conducted on both coals as well

as on high density fractions (which are predominantly pyrite) separated by a float/sink technique using bromoform (Figure 1). The much better signal/noise ratio obtained in the high density fractions as compared to the raw coals suggests that As is strongly associated with the pyrite. It is also clear that the As in the Elkhorn/Hazard coal is significantly more oxidized than in the Pittsburgh coal since the arsenate peak (A) is relatively higher than the pyrite peak (P). This is consistent with the Mössbauer analysis which indicates that a significant amount of the pyrite in the Elkhorn/Hazard coal is oxidized. Combustion experiments are planned which will explore the relationship between forms of As in the coal and As vaporization during combustion.

A previous study of trace element partitioning in two of the program coals,¹² provides an indication of the combustion behavior of trace elements in the Pittsburgh and Wyodak coals. The two coals were subjected to a leaching analysis to determine the forms of selected trace metals (As, Se, Hg, Zn, Sb, Cr). Combustion experiments and equilibrium calculations were used to understand the mechanisms governing the combustion behavior. The form of the element in the coal was shown to have major impact on the combustion behavior. Those elements that were organically bound or associated with the sulfide minerals were shown to vaporize during combustion. Once in the vapor phase, these elements in some cases reacted with minerals present in the ash to form condensed phases. The size distribution of trace elements resulting from combustion was determined by whether or not the element reacted with mineral compounds in the ash.

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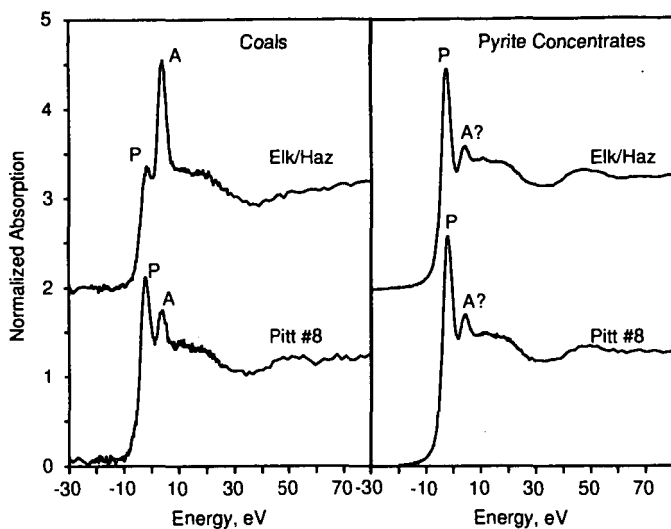


Figure 1. XANES spectra for arsenic: Pittsburgh and Elkhorn/Hazard coals and high density fractions. Peaks corresponding to arsenate (A) and pyrite-associated (P) species are indicated.

FATE OF TRACE ELEMENTS IN UK COALS DURING GASIFICATION PROCESSES

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Keywords: UK coals, gasification, pilot plant

ABSTRACT

Five UK coals were selected to cover the range of mineral matter and ash contents typically encountered in UK bituminous coals. Trace element analysis was performed on both the whole coals and size separated fractions using ICP analysis for 21 trace elements, including Be, Cr, Co, Ni, As, Cd, Sb, Hg, and Pb, elements deemed to be the most environmentally hazardous. Small quantities of each coal were gasified in a laboratory gasifier in an atmosphere of N_2 containing 15% O_2 . Samples of bed ash, cyclone ash, and a fine gas-filtered ash were collected and analysed to determine the partition of the trace elements between the gasification products. Mass balance calculations showed that the recovery of the trace elements varied from 20 to 97%; the low recovery of some trace elements highlighting the difficulties of collecting representative samples from a laboratory system.

A parallel study on samples taken from a pilot plant gasifier showed significantly higher recovery rates, indicating the value of larger scale trials.

INTRODUCTION

The gasification of coal, and in particular the development of integrated gasification combined cycles systems (IGCC) holds the promise for coal conversion processes with both higher efficiencies and lower gaseous emissions. While such systems may meet the anticipated legislation for NO_x , SO_x and particulate emissions, it is essential that the fate of the trace elements and the heavy metals which are present in all coals is well established, since these elements may yet present further environmental hazards.

Coals contain most of the naturally occurring elements with widely varying concentrations depending on rank, geological origin and history. Coal combustion has been reported as being the main source of Hg, Ni, Sn and V emissions, and the second largest source of Cd, Se, and Tl (1). The 1990 US Clean Air Act identified eleven trace elements, namely Be, Cr, Mn, Co, Ni, As, Se, Cd, Sb, Hg and Pb as being the most environmentally hazardous. These elements are all found in coals at concentrations ranging from a few ppb for elements such as Sb and Hg, to several hundred ppm for Mn. The majority of the trace elements are associated with the mineral matter in the coal. This mineral matter consists primarily of clays (aluminosilicates) and quartz, with smaller amounts of carbonates, sulphides, sulphates and oxides. Trace elements may also be associated with the macerals, reflecting the inorganic species present in the vegetation from which the coal was formed. The exchange of ions between mineral matter and macerals following the coalification process gives added complexity to establishing the distribution and mode of occurrence of the trace elements in a coal.

The occurrence of trace elements has been extensively studied and reported by Swaine (2), with recent reviews by Clarke and Sloss (3), and Davidson and Clarke (4). These reviews have concentrated on the origins of the trace elements in coal and on the wide range of analytical techniques which are now available for their determination. Pyrite in coal is generally accepted as being a major source of many of the trace elements, and in particular those of environmental concern.

During combustion or gasification of a coal the trace elements partition between the ash residues and the gaseous emissions. The actual distribution will depend on the combustion or gasification conditions and the mode of occurrence of the trace elements in the coal. Trace elements may conveniently be divided into three groups depending on their volatility and the vapour pressure of simple compounds such as oxides and chlorides. Group I elements are the least volatile and remain with the ash residues. Group II elements are more volatile and partition between the residual ash and the gaseous phase, with condensation of vapour species on the surface of the fine ash particles as the gases cool. Group III elements have a high volatility and show little or no tendency to condense from the vapour phase. Many of the environmentally sensitive elements fall into groups II and III, highlighting the current concern. Dale (5) reported on the trace element partitioning in the stack emissions from pf fired power stations, stressing the importance of monitoring flue gas discharges which may contain some of the environmentally sensitive elements. Other studies, notably those carried out by KEMA in the Netherlands (4) have shown that, with the exception of Hg and Se, 95% or more of the trace elements may be recovered from the bottom ash and the electrostatic precipitators at a power station. Concern remains that the fine particulate matter, with surface enrichment in trace

elements, may escape the gas cleaning process.

Much less work has been reported on the fate of the trace elements during gasification processes. Here the conditions are much more reducing and thus the volatile species may be different from those which form in a combustion process. Benson et al (6) reported that elements such as As, Cd, Se and Pb all showed increased volatility as the C:O ratio decreased in a laboratory gasification study of three US coals. Bushell and Williamson (7) gave the results of a trace element survey for a selection of UK bituminous coals. This showed that the elements with the strongest mineral associations were Ba, Co, Cr, Cu, La, Pb, Zn, and Zr, while those elements with a strong maceral association were Be, Sr and V.

This paper gives further details of the fate of the trace elements during gasification of coals from both a laboratory study and a pilot scale gasification process using UK coals.

EXPERIMENTAL

Five UK bituminous coals were selected from the UK Coal Data Bank, currently managed by CRE Group Ltd, Stoke Orchard. The coals provided the range of ash contents and mineralogy found in UK coals. Coals were supplied as partially washed <212 μ m coals. A high temperature ash (HTA) was prepared in a muffle furnace at 815°C and the major oxides and the trace elements present were analysed using a lithium borate fusion, followed by ICPS analysis. The elements As, Sb and Bi were determined by a hydride generation technique, and both the coals and ashes Hg was determined by a cold vapour generation process followed by ICPS.

A low temperature ash (LTA) was prepared in an O₂ plasma which left the mineral matter in a largely unaltered form. Mineral matter was identified by x-ray powder diffraction analysis of the LTA, and a quantitative estimate of the proportions of the minerals present was made by a normative analysis procedure, using the ash composition and the minerals known to be present.

Samples of each coal were ground to <38 μ m and then density separated into mineral-rich and coal-rich fractions using bromochloromethane ($\rho = 1.99\text{ g cm}^{-3}$). Each fraction was analysed for the trace elements and enrichment factors calculated, i.e. the concentration of an element in the separated fraction / concentration of the element in the original coal, to determine how the trace elements were partitioned between the macerals and the mineral matter.

Each coal was also separated into eight size fractions using a Gilsonic Siever with mesh sizes at 180, 150, 125, 106, 75, 53 and 38 μ m. Size fractions were high temperature ashed and the trace elements in each fraction determined to assess the distribution of the trace elements between the various size ranges.

The coals were gasified in a laboratory gasifier where 10 x 1g samples of coal were introduced into a pre-heated bed of fluidised sand at 950°C where the fluidising gas was 15% O₂ in N₂. After gasification, samples of the bed ash, cyclones fines and fine gas-filtered particulates (10-0.1 μ m) taken from the gas stream were analysed for the trace elements.

The fate of the trace elements in the laboratory gasifier were compared to that in a pilot plant scale gasifier. Coal and ash residues were obtained from the air-blown gasifier (ABG) operated by British Coal at the Coal Research Establishment at Stoke Orchard. This gasifier operates at temperatures up to 1000°C and 20 bars pressure, with coal feed rates of 200-300 kg hr⁻¹. Some 70-80% of the coal is converted into a low calorific gas, with ash and char being continuously removed from the base of the reactor to a circulating fluidised bed combustor (CFBC), where the remaining char conversion takes place. Limestone may be added to the coal as a sulphur sorbent to retain the sulphur in the bed ash. Samples of coal feed, bed ash and ash from the primary cyclone were provided for analysis of the major oxides and the trace elements.

RESULTS AND DISCUSSION

The ash composition and the trace element concentrations in each of the coals used for the laboratory gasification studies are shown in Table 1. To a first approximation, the concentration of most of the trace elements is related to the amount of mineral matter in the coal and thus high ash coals showed higher concentrations of the trace elements. The coals all contained mixtures of clays (kaolinite and illites), quartz and pyrite in different proportions, and variable but smaller amounts of calcite, dolomite, ankerite, rutile and apatite. Trace element concentrations were noticeably higher for coals with larger amounts of pyrite. Ash contents ranged from 3.9 wt% for the Daw Mill coal to 19 wt% for Longannet. Since Longannet has the lowest iron content, although the ash content is high, the trace element levels are still comparable with the other coals.

In general the ash contents of the size separated coals increased as the size range was reduced. The one exception to this was the Longannet coal, where the mineral matter was uniformly distributed across all the size ranges, and thus relatively uniform trace element concentrations were observed for each size fraction of the coal.

Samples of the bed ash, cyclone fines and the fine particulate ash filtered from the gas stream of the laboratory gasifier were analysed and a mass balance calculation performed to determine the distribution of the trace elements during the gasification process. The results with the Daw Mill coal (3.9 wt% ash) are shown in Table 2. With the exception of Cd and Zn, where virtually no recovery was recorded, 30 - 90% of most of the trace elements which entered the gasifier could be accounted for. Most of the trace elements were found in the cyclone fines, where the major oxide ash composition was close to that of the whole coal. A few percent of the trace elements were retained in the bed ash or found with the fine particulates filtered from the gas stream. This suggests that at the gasification temperatures most of the trace elements remain with the decomposed mineral matter, which is elutriated from the bed as the char is oxidised. Some trace elements may be volatilised under gasification conditions, to then recondense on the surface of the ash particles in or before entering the cyclone separator.

Similar results were obtained with the Longannet coal (19.0 wt% ash) as shown in Table 3. The mass balance calculations showed a higher recovery of the trace elements in the gasifier residues, with again the majority of the trace elements appearing in the cyclone fines. Significant amounts of Zn and La were found in the gas-filtered fines, which suggested that condensation of the Zn had occurred on the surface of the finest ash particles from the cooling vapours, while in addition the elutriation of very small La enriched particles (clays) from the fluidised bed may be a possible explanation of the high value for the La.

The results from the laboratory study were nevertheless disappointing, with substantial amounts of many of the trace elements unaccounted for in the mass balance calculations. The most likely source of error in the experimentation would appear to be in the sampling of the bed ash, since this is where many of the low volatile elements should appear. The difficulties in taking representative 1-2g samples from a 200g bed of sand are formidable when one realises that it may be just a few mineral grains, rich in trace elements, which are distributed somewhere in the bed. This raises the whole question of the problems and the suitability of laboratory studies for this type of research.

Residues from the British Coal air-blown gasifier consisted of a bed ash containing approximately 50% char, and fines collected from the primary, secondary and tertiary cyclones. Bed ash and primary cyclone fines constituted the bulk of the inorganic material introduced into the gasifier. Table 4. shows the distribution of the trace elements between the bed ash and the primary fines when Daw Mill coal was used as feedstock for the gasifier. An ash analysis showed that the primary fines were enriched in Fe, indicating possible preferential elutriation of fine particles of pyrite from the bed. Trace element analysis and mass balance calculations showed that 95% or more of the trace elements introduced into the gasifier could be accounted for. The trace elements partitioned relatively uniformly between the bed ash and the fines. The more volatile elements such as Be, Co, Cr, Cu, Mo, Ni, Pb, and V showing an enrichment in the fines, while the more refractory elements such as Ba, Sc, Y and Zr showed a slight preference to remain in the bed ash. The high levels of trace elements found in the cyclone fines from both the laboratory studies and the pilot scale gasification process suggests that the physical and chemical association of the trace elements with the decomposed mineral matter is perhaps as much, if not more important, than the volatility of the elements. Thus establishing the mode of occurrence of the trace elements in a given coal may be key factor in determining the fate of the trace elements on gasification.

CONCLUSIONS

Trace element concentrations in UK coals have been found to be closely related to the amount of mineral matter in the coal. In particular, many of the trace elements would appear to be associated with the pyrite. On gasification the trace elements are distributed between the residual ash and a cyclone ash, with condensation of the more volatile species on the surface of the finest ash particles. Pilot scale gasification has provided better mass balance data than the laboratory studies.

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Table 1. Ash content, trace element concentrations and mineral matter in each coal used for laboratory gasification studies.

Coal	Kellingley	Longannet	Daw Mill	Thoresby	Nadins
ash content (wt%)	4.2	19.0	3.9	4.2	9.4
SiO ₂	33.7	52.3	30.3	36.3	28.6
Al ₂ O ₃	19.5	39.7	25.9	25.3	15.7
Fe ₂ O ₃	23.9	1.4	14.4	25.5	26.4
MgO	0.8	0.5	3.2	0.7	2.9
CaO	9.6	0.9	13.7	2.1	10.6
Na ₂ O	3.6	0.2	0.8	5.6	0.3
K ₂ O	1.3	0.6	0.4	1.6	1.5
P ₂ O ₅	5.0	0.9	0.3	0.2	0.7
TiO ₂	0.8	1.5	1.0	0.9	0.6
MnO	0.2	0	0.5	0	0.3
Trace elements (ppm)					
Ag	1	0	0	0	0
As	5	1	7	12	31
Ba	67	160	150	67	64
Be	1	3	0.6	2	4
Bi	0.1	0.4	0.2	0.2	0.1
Cd	0	0	0	0	0
Co	6	11	5	3	14
Cr	10	57	11	11	28
Cu	23	61	6	24	15
Hg	0.04	<0.01	0.07	0.07	0.1
La	4	43	4	5	6
Li	6	76	7	11	15
Mo	3	4	3	4	4
Ni	13	46	11	14	52
Pb	8	21	8	21	56
Sb	1	0.4	0.3	1.8	2.4
Sc	2	-	1	2	5
Sr	53	581	35	34	44
V	16	45	15	29	25
Zn	62	27	3	13	29
Zr	10	58	8	11	11
Mineral matter content of coals (wt%)					
kaolinite	28	85	54	38	34
illites	27	11		33	
quartz	5	3			9
pyrite	28		20	29	34
calcite			14		7
apatite	12				
rutile		1			
ankerite					16
dolomite			12		

Table 2. Distribution of trace elements between bed ash, cyclone ash and gas-filtered fines from the laboratory gasification of the Daw Mill coal.

	Input to gasifier (µg)	% elements recovered	Distribution of trace elements			
			Bed ash	Fines	Filter	Balance
Ag	1.1	86	5.5	80.7	0	13.8
Ba	1413	33	2.9	29.1	0.5	67.5
Be	5.5	35	2.3	32.6	0	65.1
Cd	5.7	0	0	0	0	100
Co	44	37	2.0	35.0	0	62.9
Cr	99	34	3.3	30.4	0	66.3
Cu	80	35	3.0	31.7	0.1	65.2
La	31	43	5.7	37.7	0	56.6
Li	47	47	5.6	41.4	0	52.9
Mo	30	31	2.5	28.3	0	69.3
Ni	97	33	2.0	31.2	0	66.8
Pb	80	100	7.0	72.3	20.6	-
Sr	288	43	4.4	38.7	0.3	56.6
V	146	40	2.3	37.4	0.1	60.2
Zn	296	0.3	0	0	0.3	99.7

Table 3. Distribution of trace elements between bed ash, cyclone ash and gas-filtered fines from the laboratory gasification of the Longannet coal.

	Input to gasifier(µg)	% elements recovered	Distribution of trace elements			
			Bed ash	Fines	Filter	Balance
Ag	8.3	36	5.7	27.9	2.0	64.4
Ba	1263	67	20.9	45.7	0	3.4
Be	26	56	5.7	49.8	0.7	43.8
Cd	7.2	52	11.0	39.7	1.0	48.3
Co	91	57	2.4	53.9	0.7	43.1
Cr	387	56	3.7	51.5	0.9	43.9
Cu	502	56	4.0	50.9	0.8	44.3
La	305	84	3.3	50.6	30.7	15.5
Li	642	68	17.1	50.4	0.4	32.2
Mo	31	48	5.2	41.5	1.7	51.6
Ni	384	63	11.0	50.7	0.8	37.5
Pb	154	64	12.1	47.1	5.0	35.8
Sr	4392	67	14.3	50.7	1.9	33.2
V	442	60	5.4	54.5	0.5	39.7
Zn	160	54	11.4	35.0	7.9	45.7

Table 4. Distribution of trace elements between bed ash and primary cyclone fines using Daw Mill coal in the pilot scale air-blown gasifier

Trace element input (mg.hr ⁻¹)		Output of trace elements (mg.hr ⁻¹)			Distribution of trace elements	
		bed ash	Fines	Unaccounted	Bed ash (%)	Fines (%)
Ag	0.16	0.03	0.04	0.09	40	60
Ba	97	57	48	0	54	46
Be	0.25	0.05	0.11	0.09	32	68
Cd	0.17	0.05	0.04	0.08	51	49
Co	1.3	0.42	0.82	0.09	34	66
Cr	4.3	1.2	2.3	0.85	35	65
Cu	4.1	1.0	2.7	0.35	27	73
La	1.3	0.48	0.76	0.08	39	61
Li	3.8	1.6	2.0	0.24	44	56
Mo	0.64	0.17	0.48	0	26	74
Ni	4.5	1.2	2.4	1.0	33	67
Pb	3.7	0.54	1.3	1.32	29	71
Sc	0.91	0.14	0.05	0.72	73	27
Sr	11	2.6	6.3	2.04	29	71
V	5.2	1.9	3.9	0	32	68
Y	1.8	2.2	0.1	0	96	4
Zn	3.1	3.0	1.7	0	63	37
Zr	9.1	12.3	0.19	0	98	2

THE BEHAVIOR OF TRACE ELEMENTS IN FLUIDIZED BED COMBUSTION

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ABSTRACT

The present study focuses on the behavior of major, minor and trace elements during fluidized bed coal combustion, at 850°C in a 0.14 m i.d. atmospheric reactor. The combustion ashes were continuously taken out of the bed. The rest were elutriated by the combustion gases and collected in two cyclones and a baghouse filter located at the outlet. A low volatile bituminous coal from the Asturian Central basin (North of Spain) was used for the experiments that comprised two tests; with and without addition of limestone. The concentrations of 57 elements were determined in the coal and in the different combustion ashes by ICP-MS, ICP-EAS, and XRF. Elements normally present in the combustion flue gases as vapor, such as Hg and As were sampled in impingers, and determined by cold vapor atomic absorption, and ISO R-601 standard method. Using these methods these elements were not detected in the gas phase. No major differences were observed on the behavior of trace elements during combustion with and without limestone addition. The results show a clear grain size segregation of elements of environmental concern such as As, Co, Cu, Hg, Mo, Ni, Pb, Sb and Se. These elements are enriched in the finest grain size fraction. The grain size partitioning could be attributed to the following processes: a) physical segregation of major and trace elements in the reactor, due to differences on the distribution of these elements in the feed coal and, b) chemical segregation due to volatilization and condensation from flue gas.

INTRODUCTION

Information about of relative contribution of "hazardous air pollutants" trace elements to the atmospheric emissions from coal combustion is important to evaluate the environmental impact of these contaminants. Future environmental regulation of these emissions will be more stringent. During pulverized coal combustion (PCC), trace elements are partitioned between the bottom ashes, fly ashes and vapor, according, not only to the operating conditions and furnace design, but also to their mode of occurrence. This mode of occurrence differs in coals from different origins. Trace element partitioning in PCC has been extensively studied and although there are some aspects related to their behavior that need to be clarified, some generalizations have been established¹⁻⁶. A relative enrichment of trace elements in fly ashes, specially in the fine grain size fractions due to condensation of volatile species from the flue gases on the surface of fly ash particles has been found¹⁻⁶.

The fate of trace elements during fluidized bed combustion (FBC) has received less attention and information in the literature is scarce. It can be assumed that trace elements volatilization at the typical fluidized bed combustion temperatures (<900°C) will occur in less extension than in pulverized coal combustion (>1400°C). However, the expected reduction of trace element emissions in FBC could be partially offset by the longer residence times. Experimental data on the behavior of trace elements in FBC are inconclusive and depend on the type of coal and operating conditions. Most of the measurements of trace elements emissions from FBC have been obtained in atmospheric plants but some data are available for pressurized fluidized bed combustion⁷. Regarding the operating conditions, it has been observed that trace element emission in FBC can be reduced by changing the depth of the bed^{3,8}. Thus, when the bed depth is reduced to half, emissions of selected trace elements decrease between 5% and 50%. When comparing the trace element behavior for PCC and FBC some differences have been found. For instance, it has been observed that in FBC systems, emissions of elements such as Hg, As, Pb, Sc, Co, Na and K are lower than in PCC¹, even be below the emission standards⁹. The enrichment of volatile elements in the finest ash particles, which occurs regularly in PCC, does not happen in some FBC systems¹⁰. However in other studies^{3,11} it has been observed that trace element concentration increases with decreasing particle size. It should also be remarked that in some tests, Hg was the only element detected in the gas phase in flue gases from FBC³, whereas in PCC other elements such as B, Cl, F, Se and As were frequently present. The effect of limestone, added to control of SO₂ emission, upon trace element behavior is not clear. Thus, it has been observed that As, Cd, Pb, and Se emissions were significantly reduced with limestone addition². In the other hand, it has been reported that addition of limestone gave rise to an increase in Pb, Cd and Mn emissions, which was justified by the likely presence of these elements in the limestone³. In a study carried out in PFBC, it has been concluded that trace elements emissions with or without limestone addition is similar⁷.

With the aim of contributing to the knowledge of the behavior of trace elements during fluidized bed combustion, in the present work, experiments with and without limestone addition, were carried out.

EXPERIMENTAL PART

Coal combustion was carried out in a laboratory-scale continuous fluidized bed reactor (0.14 m i.d.). The coal, ranging in size from 0.16 to 1.5 mm, was fed continuously. Most of the ashes were continuously taken out of the bed. The rest were elutriated by the combustion gases and collected in two cyclones and a baghouse filter placed in the outlet. The experiments were carried out with a fluidization velocity of 0.7 m/s, an air excess of 30% and at combustion temperature of 850°C.

The sampling train for recovering trace elements from flue gases, was similar to the equipment specified by the US Environmental Protection Agency (EPA). The reagent used in the impingers was 0.5 M HNO₃. The content of Hg and As in this solution were determined by cold vapor atomic absorption spectrometry, and the ISO R-601 standard method.

A low volatile bituminous coal from the Asturian Central basin (North of Spain) was used in this study. The proximate, elemental analyses and sulfur forms are given in Table 1. The concentrations of 57 elements in the coal, ashes from the bed (R), from the two cyclones (C1 and C2), and from the baghouse filter (BF), were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Emission Spectrometry (ICP-AES). A special two stage sample digestion method¹² for ICP analyses was used in this study in order to avoid the loss of volatile elements during sample treatment. Because sample preparation for ICP analysis involves digestion with HF, the Si content was determined by X-ray fluorescence spectrometry (XRF). Particle size distribution of the collected ashes was measured in a Counter Coulter apparatus. In order to analyze the effect of limestone addition upon the trace element emission, an experiment was carried out with limestone (coal/limestone weight ratio: 37). The limestone was fed into the reactor in sizes between 0.1 and 0.5 mm. This limestone sample does not contain significant trace element concentration with the exception of 1589 ppm of Sr.

RESULTS AND DISCUSSION

The concentrations of major, minor and trace elements in the coal and combustion ashes R, C1, C2 and BF are given in Table 2. Concentrations in the coal have been referred to ashes in order to normalized the results. Major and minor elements have been also determined in order to ensure a balance of volatile and non-volatile elements during the experiments. The accuracy of the mass balance depends upon the ash sampling in the reactor which involves some errors, but roughly allows to estimate that elements such as As, Be, Cd, Hg and Se, could be partially released in vapor phase or condensed in the cold parts of the system. In spite of that, Hg and As analyzed in the flue gases by the methods already described, were not detected in the gas phase. The concentration of most of the trace elements decreases in the bed ashes (R) and increases in the fly ashes, mainly in those from the C2 and BF. This segregation could be attributed to two different processes: one is the physical segregation of major and trace elements in the reactor due to differences on the distribution of these elements in the feed coal and the other, the chemical segregation due to volatilization and condensation from flue gas.

In a previous work, mineral matter composition in this coal has been analyzed¹³. Illite, chlorite, kaolinite, quartz, pyrite, calcite, dolomite and siderite were the major minerals identified. After coal combustion in the FBC, illite and quartz remained mostly unaltered in the ashes but the other phases were transformed in oxides and sulfates¹³. We should kept in mind that some of these minerals, are dispersed as fine particles of inherent mineral matter. Moreover, when the coal particles are burnt at the temperatures used in FBC (i.e. 850°C) some particles of mineral matter retain their original size or can be fragmentate. The mineral species of finest particle sizes are preferentially elutriated with the flue gases and a depletion of their concentration in the R ashes is expected. Concerning to the major elements (Table 2), this depletion is more significant for the elements present as carbonates (Ca, Mg, Fe), and also occurs for trace elements with carbonate affinity, such as Ba and Sr.

In the other hand, volatile trace elements are preferably concentrated in the fly ash particles. This behavior is more remarkable for some elements such as As, Co, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sr and Zn. The study of the particle size distribution in R, C1, C2 and BF ashes, has shown that the C1 ash particles have reached sizes up to 60 µm, although 90% of the total volume of this particles are smaller than 8 µm. Maximum size particles found in the C2 ashes are of 15 µm, 90% of the total volume being smaller than 2 µm, and in the BF the maximum size is of 10 µm but 90% of the volume is smaller than 2 µm. The study of the enrichment of some trace elements on finest fly ash particles is of special interest. In order to eliminate the variability of different ash product characteristics, the enrichment factors (EF) were normalized to the concentration of Al. The EF of an element x is related to the concentration c of Al in coal ashes or combustion ashes as follows:

$$EF = \frac{(C_x / C_{Al})_{\text{combustion ashes}}}{(C_x / C_{Al})_{\text{coal ashes}}}$$

Enrichment factors calculated for some trace elements of major environmental concern, in the experiments with and without limestone addition, are shown in Figure 1. The rest of the elements studied, can be classified in three groups according to the EF values, in a similar way that has been done for PCC systems¹⁻³. (I) low volatile trace elements are those with no significant enrichment or depletion in all the ashes (R; C1; C2 and BF). Cs, Ga, Ge, Nb, Sc, Ti, Tl, V, Zr, and rare earth. (II) elements that vaporize during combustion and condense on the surface of the smaller fly ash particles (mainly in C2 and BF). As, Bi, Co, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, Sr, W and Zn are in this group, (III) elements that remain mostly in the vapor phase, that have enrichment factor <1 in all the ashes. Be and Cd follow this behavior. Other elements that are included normally in this group such as Hg or Se, were in part retained in the ashes.

The comparison between the composition of the ashes obtained from the tests carried out with and without limestone addition, has shown that retention efficiencies for most elements are similar in both cases. We should note that most of the Ca from the added limestone is retained mainly in R and C1, but in C1 in less extension. Particles rich in Ca, elutriated with the more fine fly ashes (C2 and BF), belong mainly to the carbonates originally present in the coal. Some elements such as Fe, Co, Cu, Sn and Zn are more concentrated in the fly ashes obtained with limestone addition. This

fact cannot be explained in terms of particle size and vaporization-condensation mechanism, such as has been done in other similar experiments³. According to the results of the Coulter Counter analysis, the size distribution of C1, C2 and BF obtained during the test carried out with limestone addition is similar to the size distribution in the test without limestone addition.

ACKNOWLEDGMENTS

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Table 1- Analyses of coal

	content wt %
<i>Proximate (db)</i>	
Volatile Matter	9.62
High Temperature Ashes	31.1
<i>Elemental (db)</i>	
C	62.1
H	2.69
N	0.96
S <i>total db</i>	0.60
O (by diff.)	2.55
<i>Other (db)</i>	
Spyritic	0.21
Sulfate	0.02
S <i>organic</i> (by diff.)	0.37
CO ₂ (from CO ₃ ²⁻)	1.77

Table 2.- Element concentrations in the ashes obtained in the experiences carried out without and with limestone addition, analyzed by Inductively Coupled Plasma Mass Spectrometry (1), Inductively Coupled Plasma Emission Spectrometry (2), or both (3). Concentrations are in ppm except for those indicated.

	coal ashes	withouth limestone				with limestone			
		R	C1	C2	BF	R	C1	C2	BF
Ag ¹	5.6	2.2	5.9	3.8	2.6	1.8	4.8	2.5	2.0
Al ² %	15.2	14.9	13.7	15.2	15.8	13.2	12.8	15.2	14.5
As ¹	48	18	57	98	93	24	46	86	69
B ³	52	41	90	87	64	39	76	80	113
Ba ³	860	678	973	1471	1714	573	880	1428	1483
Be ¹	32	13	23	17	17	12	20	16	15
Bi ¹	0.98	1.0	0.80	1.7	1.4	0.60	0.51	1.1	1.2
Ca ² %	3.73	2.40	7.00	4.91	4.37	5.68	8.35	5.15	4.19
Cd ¹	3.0	1.2	2.8	2.2	1.9	1.1	1.8	1.7	2.2
Co ¹	40	24	53	67	82	22	49	65	117
Cr ²	140	144	163	181	183	127	163	201	203
Cs ¹	23	22	17	19	19	17	15	17	16

Table 2 (cont.).-

	coal ashes	without limestone				with limestone			
		R	C1	C2	BF	R	C1	C2	BF
Cu ³	76	55	96	75	108	53	92	80	169
Fe ² %	4.50	3.75	5.48	5.20	5.57	3.41	5.13	5.15	8.82
Ga ¹	47	41	37	43	42	34	34	39	36
Ge ¹	7.3	4.3	6.1	4.3	6.4	3.5	5.5	5.4	5.7
Hf ¹	5.3	3.6	3.4	4.0	4.0	2.5	3.2	3.4	3.7
Hg ¹	0.68	0.23	0.38	4.0	3.5	0.33	0.57	4.0	3.5
K ² %	3.37	3.52	2.60	2.76	2.86	3.07	2.46	2.80	2.63
Li ²	257	219	253	282	291	199	234	263	269
Mg ² %	1.05	0.90	1.22	1.18	1.17	0.84	1.18	1.17	1.04
Mo ¹	8.7	3.0	13	20	21	4.0	12	19	21
Na ² %	0.54	0.56	0.51	0.55	0.55	0.49	0.48	0.55	0.52
Nb ¹	35	27	29	31	35	22	27	29	30
Ni ³	100	66	105	132	160	57	102	159	195
P ² %	0.03	0.04	0.05	0.07	0.04	0.03	0.04	0.05	0.07
Pb ³	84	73	80	125	131	68	62	122	114
Rb ¹	247	184	175	156	155	155	162	156	142
S ² %	1.52	0.57	1.92	2.03	1.78	1.04	1.67	1.96	1.78
Sb ¹	4.2	2.9	5.3	6.8	7.7	2.5	4.8	6.3	6.7
Sc ¹	48	33	42	46	47	30	41	42	37
Se ¹	23	5.3	19	25	24	6.6	29	24	22
Si %	23.1	23.0	20.5	-----	20.7	24.4	20.3	-----	19.6
Sn ¹	15	12	12	54	19	8	13	283	36
Sr ¹	371	280	566	795	924	374	572	773	808
Ta ¹	14	1.6	2.7	3.5	2.8	0.97	1.8	1.6	1.4
Tc ¹	1.0	0.29	0.19	0.82	0.68	0.21	0.38	0.45	0.68
Ti ² %	0.62	0.60	0.56	0.61	0.66	0.54	0.53	0.61	0.61
Tl ¹	1.3	1.4	1.2	1.6	1.3	0.95	1.1	1.1	0.87
V ³	267	192	227	227	238	171	209	220	216
W ¹	8.1	3.9	6.9	7.3	8.1	2.9	4.9	6.1	15
Y ¹	47	31	48	56	62	27	46	53	53
Zn ²	160	136	216	227	319	136	185	278	434
Zr ¹	144	87	100	102	114	70	94	99	97
Ce ¹	144	98	112	101	114	80	100	97	101
Dy ¹	8.8	6.7	9.6	11	12	5.1	8.1	9.5	9.8
Er ¹	4.9	3.2	4.7	5.5	5.5	2.4	3.9	4.5	4.9
Eu ¹	2.7	2.4	2.8	3.3	3.5	1.8	2.1	2.8	2.8
Gd ¹	12	10	11	13	15	7.2	10	11	12
Ho ¹	1.6	1.4	1.8	2.4	2.3	0.95	1.5	1.8	1.9
La ¹	74	63	63	68	75	54	56	65	67
Nd ¹	62	53	52	55	65	42	45	54	56
Pr ¹	18	17	14	17	20	13	13	16	17
Sm ¹	12	10	12	13	14	8	10	11	12
Tb ¹	1.7	1.5	1.9	2.3	2.2	1.1	1.5	1.7	1.8
Th ¹	32	27	26	27	31	21	23	26	28
U ¹	6.8	4.9	6.3	6.4	8.4	4.3	5.5	6.5	6.8
Yb ¹	4.7	3.2	4.4	4.4	4.7	2.3	3.5	3.7	3.9

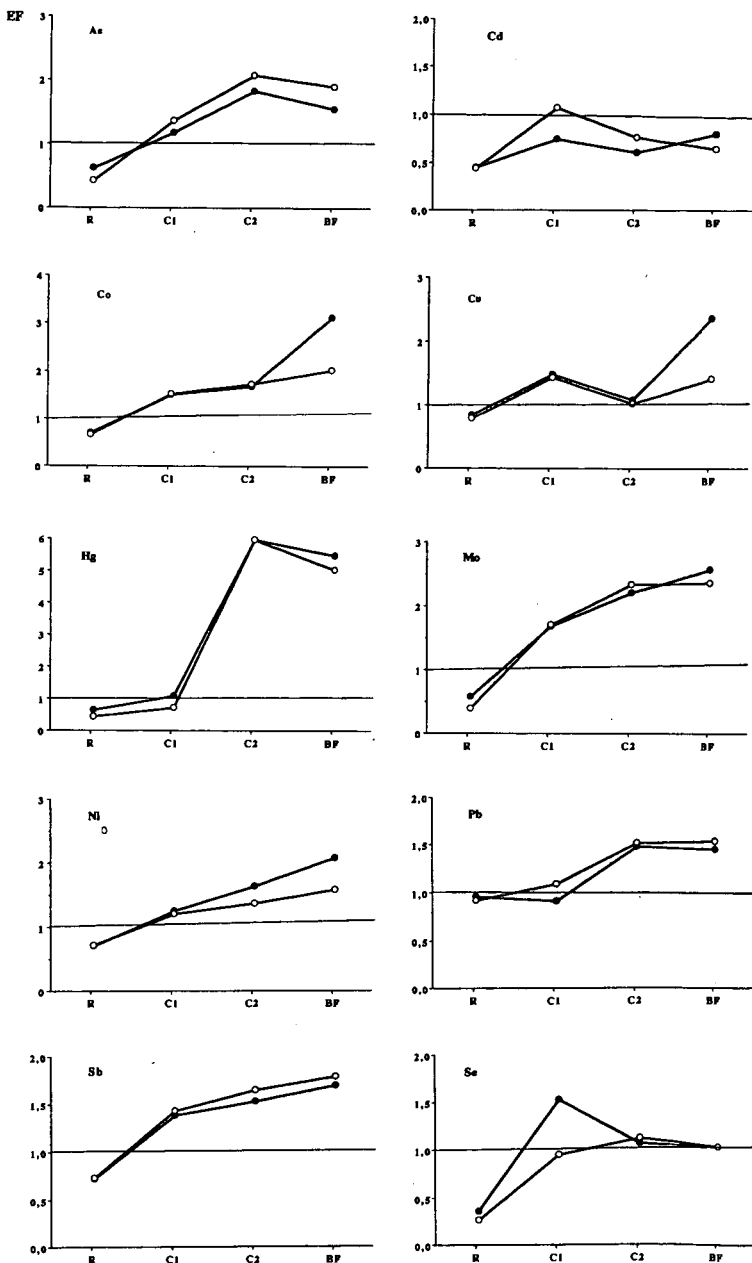


Figure 1. Enrichment factors EF for the ashes taken from the bed (R), cyclones (C1 and C2) and baghouse filter (BF), in the experiences with (●) and without limestone (○).

TRACE METAL CAPTURE BY VARIOUS SORBENTS DURING FLUIDIZED BED COAL COMBUSTION

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Keywords: Coal Combustion, Fluidized Bed, Trace Metals

INTRODUCTION

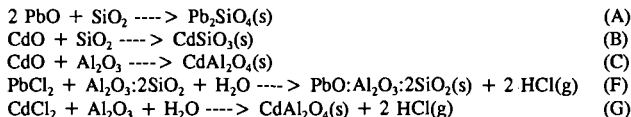
Toxic trace metallic elements such as arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium are usually contained in coal in various forms and trace amounts. These metals will either stay in the ash or be vaporized during high temperature combustion. Portions of the vaporized metals may eventually be emitted from a combustion system in the form of metal fumes or particulates with diameters less than 1 micron, which are potentially hazardous to the environment (1).

Current practice of controlling trace metal emissions during coal combustion employs conventional air pollution control devices (APCDs), such as electrostatic precipitators and baghouses, to collect fly ash and metal fumes. The control may not always be effective on metal fumes due to their extremely fine sizes (2).

This study is to explore the opportunities for improved control of toxic trace metal emissions from coal-fired combustion systems. Specifically, the technology proposed is to employ suitable sorbents to (1) reduce the amount of metal volatilization and (2) capture volatilized metal vapors during fluidized bed coal combustion. The objective of the study was to investigate experimentally and theoretically the metal capture process.

POTENTIAL METAL-SORBENT REACTIONS

The following reactions between metals and sorbent constituents have been confirmed both theoretically and experimentally (3,4,5):



EQUILIBRIUM CALCULATION

In this study, combustion equilibrium was calculated using a PC-based computer software package (6) especially developed for predicting equilibrium compositions during fuel or waste combustion. The simulation would reveal potential metal-sorbent reactions for the proposed metal capture process.

EXPERIMENTAL

Metal capture experiments were carried out semi-batchwise in a 25.4 mm (1") OD quartz fluidized bed coal combustor enclosed in an electric furnace. The metals involved in the study were cadmium, chromium and lead. Three coal samples from the Illinois Basin Coal Sample Bank (IBCSB) and an artificially prepared metal-containing wood sample were tested in the experiments. The corresponding concentration of chlorine, sulfur, and the target metals in each sample is summarized in Table 1. The sorbents tested included bauxite, zeolite and lime. The chemical composition and fluidization properties of the sorbents are listed in Table 2.

For an experimental run, a bed of sorbent was preheated to the desired temperature under the designed operating conditions. A predetermined amount of coal or wood pellets was then charged in the bed at a constant feed rate for combustion. After the combustion was completed, the bed residue was discharged for analysis of metal concentration. The experimental parameters and operating conditions associated with the experiments are shown in Table 3. Metal concentration in the coal, wood pellets, original sorbent, and combustor residue was determined by an atomic absorption spectrophotometer. An HF modified EPA Method 3050 was used to digest metals from the sorbent, which involves the use of HNO₃, HCl and HF acids (7).

RESULTS AND DISCUSSION

Simulation Results

Equilibrium calculations were performed to identify thermodynamically preferred metal speciation in a combustion system. A typical set of simulation results indicating potential lead-sorbent reactions and the effect of sulfur on lead capture by sorbents are shown in Table 4. The corresponding elemental composition and combustion conditions used in the simulations were: carbon - 71.3 wt%, hydrogen - 5.2 wt%, nitrogen - 1.4 wt%, oxygen - 12.4 to 7.8 wt%, sulfur - 0 to 4.6 wt%, lead concentration - 50 ppm, ash - 9.3 wt%, combustion temperature - 900°C, and percent excess air - 50%.

Experimental Results

Typical experimental results indicating the effectiveness of metal capture by various sorbents are shown in Tables 5, 6 and 7 for lead, cadmium, and chromium, respectively. The combustible materials tested were three coal samples, i.e., IBC-110, IBC-111 and IBC-112, and a wood sample. The sorbents used were bauxite, zeolite and lime. It is essential to point out that, due to the non-uniformity and trace-quantity nature associated with the process, it is still difficult to discuss the effect of fuel type, coal type, and coal properties such as chlorine, sulfur, ash and metal contents on the metal capture process based on the current results. Additional experiments are being carried out to provide more statistically representative results for better understanding the metal capture process.

CONCLUSIONS

This study investigated the possibility of employing suitable sorbents to capture toxic trace metals during fluidized bed coal combustion. The observed experimental results indicated that metal capture by sorbents can be as high as 91% depending on the metal species and sorbent involved. All three sorbents tested, i.e., bauxite, zeolite and lime, were observed to be capable of capturing lead and cadmium in a various degree. Zeolite and lime were able to capture chromium. Results from equilibrium simulations suggested the formation of metal-sorbent compounds such as $Pb_2SiO_4(s)$, $CdAl_2O_4(s)$ and $CdSiO_3(s)$ under the combustion conditions.

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Table 1. Concentration of Chlorine, Sulfur and Target Metals in Tested Coal Samples and Wood pellets (Units: ppm for metals, % for Cl and S)

Species	IBC-110	IBC-111	IBC-112	Wood*
Cd	<0.4	<0.4	<0.3	5
Cr	11	14	14	20
Pb	10	18	27	30
Cl	0.0%	0.0%	0.2%	0.0%
S	4.6%	2.0%	2.8%	0.0%

*Spiked Metals: Metal Nitrates

Table 2. Major Composition, Trace Metal Concentration and Fluidization Properties of the Three Tested Sorbents

Composition or Property	Bauxite	Zeolite	Lime
SiO ₂ (%)	9.0	66.7	0.7
Al ₂ O ₃ (%)	78.0	12.1	0.3
CaO (%)	0.0	3.1	97.2
Cd (ppm)	3.0	1.3	2.5
Cr (ppm)	286	3.5	4.5
Pb (ppm)	51.8	22.0	25.2
<hr/>			
d _p (mm)	0.5	0.5	0.5
U _{mf} (cm/s)	3.8	3.5	3.8

Table 3. Experimental Parameters and Operating Conditions

Parameter	Range
Fuel Type	Coal, Wood
Coal Size	2.0 - 2.8 mm
Wood Size	4.8 mm
Fuel Amount	60 g
Fuel Feed Rate	0.22 g/min
Sorbent Type	Bauxite, Zeolite, Lime
Sorbent Size	0.4-0.6 mm
Sorbent Amount	22.5-30 g
Static Sorbent Height	6 cm
Air Flow Rate	3 U _{mf} of Sorbent
Combustor Temperature	900°C
Combustion Duration	4.5 hrs

Table 4. Equilibrium Simulation Results for Lead with or without Sulfur

Sorbent Constituent	Metal	With or Without Sulfur	Sulfur-Metal-Sorbent Compound
SiO ₂	Pb	Without S	Pb ₂ SiO ₄ (s) < 1000°C
			PbO(g) > 1000°C
		With S	PbSO ₄ (s) < 950°C
			Pb ₂ SiO ₄ (s) < 1000°C
			PbO(g) > 1000°C
Al ₂ O ₃	Pb	Without S	PbO(s) < 900°C
			PbO(g) > 900°C
		With S	PbSO ₄ (s) < 950°C
			PbO(g) > 950°C
CaO	Pb	Without S	PbO(s) < 900°C
			PbO(g) > 900°C
		With S	CaSO ₄ (s) > 500°C
			PbSO ₄ (s) < 950°C
			PbO(g) > 950°C

Table 5. Percentage Lead Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	68	60	27
Coal (IBC-111)	58	91	51
Coal (IBC-112)	66	51	21
Wood Pellets	48	52	53

Table 6. Percentage Cadmium Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	66	64	43
Coal (IBC-111)	74	21	57
Coal (IBC-112)	72	84	21
Wood Pellets	14	36	8

Table 7. Percentage Chromium Capture by Sorbents (%)

Fuel Type	Bauxite	Zeolite	Lime
Coal (IBC-110)	0	57	8
Coal (IBC-111)	0	19	5
Coal (IBC-112)	0	17	12
Wood Pellets	0	33	34

TRACE ELEMENTS OF PETROLEUM - FCCU FEEDSTOCK, FRESH, SPENT AND DEMETALLIZED FCCU CATALYST SOLIDS & LEACHATES; DEMETALLIZATION REDUCES LEACHABILITY, INCREASES STABILITY

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Trace elements contaminate Fluid Catalytic Cracking Unit (FCCU) catalysts by blocking pores and catalyzing steam deactivation. Elemental analyses of catalyst solids and leachates are necessary to characterize the system. Demetallization removes a portion of contaminants by pyrometallurgical and hydrometallurgical procedures. Catalysts were leached by various methods and IAW TCLP. Demetallized catalyst TCLP leachates are below the UTS TCLP limits proposed September 14, 1994, for all fourteen elements. Immediate catalytic activity improvement and improved resistance to steam deactivation is shown micro-activity (MAT) tests before and after severe steaming.

Fluid Catalytic Cracking is a valuable refining process to upgrade heavy hydrocarbons to high valued products (Avidan, 1993). Through the cycles of cracking, fresh catalyst deactivation is caused by contaminant blockage of active sites (nickel, vanadium, iron, et al.) and by steam catalyzed by contaminants, e.g. vanadium, sodium, et al. (Pine, 1990; Pavel, 1992). To compensate for decreased FCC feedstock conversion and product selectivity, a portion of the circulating catalyst equilibrium inventory is withdrawn for spent catalyst disposal, and fresh catalyst is added to the system (Habib, 1979).

Spent FCCU catalyst disposal quantities have been published in various formats, and disposition alternatives include those "options which recover metals: 1) On-site demetallization and recycle for FCCU catalysis -- on-site source reduction ⁽¹³⁾; 2) Off-site demetallization and recycle for FCCU catalysis -- original application recycle ⁽¹⁴⁾; 3) Off-site spent catalyst (ultra-low metals) sale to others ⁽¹⁶⁾ for further metals loading, a limited market at equilibrium which requires disposal by others and does not affect disposal of total replacement volumes of fresh catalyst sold, and the metals deposited from feedstocks. 4) Off-site demetallization for metals recovery prior to secondary use or disposal ⁽¹⁷⁾; 5) Other waste treatment technologies prior to disposal, e.g. solidification, stabilization, vitrification, cementation, etc. ⁽¹⁸⁾; 6) Cement kilns, with or without pretreatment, either 6a) cement kilns permitted/licensed for hazardous wastes, or 6b) cement kilns blending wastes as alternative feed stocks ^(16,19); 7) Landfills ^(11,12,16,19)" (Pavel, 1995)

Trace elements enter the FCCU system from feedstocks, fresh catalysts, feedstock and/or catalyst additives. Analyses of petroleum by Filby, Yen, Shah, et al. (Yen, 1975), showed a wide range of elements in petroleum. The feedstock to FCCUs typically includes the gas oil fraction, between diesel and asphalt, and in some cases all of the long residue with a boiling point above diesel. Refiners normally analyze FCCU feedstock for C and S and occasionally N, for Ni and V fairly often, sometimes seldom analyze for more than Ni, V, and in some cases, Na, Fe. ICP elemental analyses for several feedstocks are shown in Table 1. Elemental analyses of spent Fluid Catalytic Cracking (FCC) catalyst solids and leachates are necessary to characterize the total FCC catalyst system including yield impacts and environmental considerations.

Catalyst and leachate analyses: Elemental analyses of solids and leachates were performed using ICP and XRF, analyses of leachates were performed by ICP. Table 2 shows a representative catalyst test set which includes a fresh, spent, and demetallized spent catalyst. Toxicity Characteristic Leaching Procedures (TCLPs) were performed in accordance with EPA standard methods, and results were compared to the proposed Universal Treatment Standards, Land Disposal Restrictions -- Phase II (LDRII), published September 19, 1994. Additional leach tests were performed with deionized water flushed (DIF) through catalyst using 20 parts water to 1 part catalyst. Demetallized catalyst TCLP leachates are below the UTS for all elements including vanadium (Pavel, 1994). New pyrometallurgical and hydrometallurgical controls and procedures further improve metal removal and enhance catalytic properties. Immediate activity improvement is seen in MATs prior to steaming. Improved resistance to steam deactivation, catalyzed by vanadium and other elements, is shown after spent and demetallized spent catalyst were steamed for 4 and 16 hours at 1450°F, and then ASTM microactivity (MAT) tested.

Demetallization processing (DEMET) takes a portion of spent FCC catalyst, removes a portion of metal contaminants by pyrometallurgical (calcining, sulfiding, nitrogen stripping, chlorinating) and hydrometallurgical (leaching, washing, drying) procedures, to return the base demetallized spent catalyst to the FCC. Standard demetallization has most frequently utilized 1450°F calcining and sulfiding with 650°F chlorinating. Off-gases from reactors are scrubbed (Elvin, 1993). Contaminant metals are precipitated and filtered for disposal in the same manner used for spent catalyst, or they can be shipped to a Best Demonstrated Available Technology recycler of metals, depending on the client preference or regulatory environment. The operation of one unit for one refiner has resulted in the recycle of over 15,000 tons of spent FCC catalyst back to the FCC. Demetallized spent FCC catalyst recycle has reduced the requirements for fresh catalyst additions and reduced generation of catalyst fines. DEMET processing removes contaminants known to be detrimental to conversion, product selectivities, and mechanical performance of the FCC. With DEMET capacity sized to reduce metals levels on circulating catalyst, yields could be improved due to lower metals on circulating catalyst.

New DEMET procedures improve metal removal, initial activity and hydrothermal stability. Standard DEMET processing utilizes a series of pyrometallurgical and hydrometallurgical procedures for metal removal. By removal of contaminants, access channels to active sites are renewed. Care is taken during processing to maintain the catalyst integrity and hydrothermal stability. New advancements in sulfidization and aqueous processing have further improved metal removal and demetallized spent catalyst characteristics of high initial activity, and low hydrothermal deactivation rates.

Table 1. FCCU Feedstock Elemental Analyses (ppm) by ICP

Element	Feed1	Feed2	Feed3	Feed4	Feed5	Feed6	Feed7
Aluminum	2.9	38.7	0.4	1.6	4.8	nt	0.5
Antimony	0.2	2.1	1.1	0.2	0.2	<0.2	<0.2
Barium	nt	nr	0.9	<0.1	<0.1	nt	<0.2
Beryllium	nt	nt	nt	nt	nt	nt	nt
Bismuth	0.6	bdl	<0.1	0.2	0.2	<0.2	<0.2
Boron	<0.1	4.3	<0.1	0.7	<0.1	nt	<0.2
Calcium	19.9	15.3	1.6	2.7	0.5	0.4	0.5
Carbon	nr	nr	1.4	7.8	4.4	2.2	4.8
Cerium	0.2	nr	<0.1	<0.1	<0.1	nt	nt
Chromium	0.6	nr	<0.1	<0.1	<0.1	<0.2	<0.2
Copper	0.2	0.4	0.2	0.1	<0.1	<0.2	<0.2
Iron	14.3	16.6	5.2	16.0	7.6	3.4	5.3
Lanthanum	0.1	nr	<0.1	<0.1	<0.1	nt	nt
Lead	0.3	2.4	0.1	0.3	0.6	<0.2	<0.2
Magnesium	2.5	3.5	2.6	1.0	0.1	0.2	0.3
Manganese	0.2	0.1	<0.1	0.1	<0.1	<0.2	<0.2
Neodymium	<0.1	nr	<0.1	<0.1	<0.1	nt	nt
Nickel	2.2	4.8	3.4	22.0	3.9	13.0	12.1
Phosphorus	0.7	2.3	0.6	0.1	0.2	<0.2	<0.2
Potassium	0.6	5.7	0.6	0.5	0.7	nt	<0.2
Praseodymium	<0.1	nr	<0.1	<0.1	<0.1	nt	nt
Selenium	nt	bdl	<0.1	0.2	0.2	nt	<0.2
Silica	nt	nt	nt	nt	nt	nt	nt
Sodium	21.4	27.4	1.4	28.0	1.2	2.1	0.5
Strontium	0.6	nr	<0.1	<0.1	<0.1	<0.2	<0.2
Sulfur	nr	nr	1.3	1.2	0.3	0.13	0.37
Tin	0.1	0.4	0.7	0.5	0.7	<0.2	0.8
Titanium	0.1	0.7	<0.1	0.1	<0.1	<0.2	<0.2
Vanadium	3.5	4.3	2.4	40.0	6.5	0.9	8.6
Zinc	0.9	2.6	0.4	1.2	0.3	nt	<0.2
Zirconium	<0.1	nr	0.1	<0.1	<0.1	nt	<0.2

note: "nt" indicates "not tested" at the time of that sample; "nr" indicates "not reported"

Improved metals removals are accomplished primarily during the pyrometallurgical steps of processing. Special DEMET procedures were developed by rigorous thermodynamic modeling of the sulfidation environment to ensure the reaction mix and temperature appropriate to convert available contaminant oxides to sulfides (Pavel, 1993). Accurate analyses of all contaminant elements (not just nickel and vanadium) are required for accurate modeling. Improved metals removal enables more efficient utilization of hardware and provides the ability to lower metals on circulating catalyst. Improved metals removal shows that more sites have been uncovered, and micropore channels leading to active catalytic sites restored.

Elements not tested and/or reported in the following tables, but often found on catalysts include three groups. Elements most typical, but not tested and/or reported: Carbon, Chlorine, Hafnium, Hydrogen, Nitrogen, Oxygen, Scandium. The second group accounts for the rare earth mix supplied fresh catalyst manufacturers which includes the four reported plus Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Terbium, Ytterbium, Lutetium. The third group includes elements found in crude and on occasion various catalysts: Fluorine, Iridium, Osmium, Palladium, Platinum, Rhenium, Rhodium, Ruthenium. All tests have been performed by third party laboratories. The demetallization procedure used was for recycle of spent demetallized catalyst, alternative procedures would be utilized if processing for any other purposes. When some elements are removed, the elements remaining might appear to increase as a portion of the total remaining material. The list of elements is extensive, but not complete, as elemental testing includes over 70 elements.

Every FCCU feedstock, hardware, and catalyst system are unique. Some systems have more elements than in the following table (Table 2).

Improvements in hydrothermal stability and additional activity for recycle to the FCC are achieved through the hydrometallurgical processing steps. Special DEMET procedures were developed by rigorous modeling of solution properties during the wash step (Pavel, 1993). Additional proprietary steps are incorporated in the washing prior to drying on the belt filter. Aqueous processing modifications resulted in a number of attractive alternatives which can be selected through regulating variables in a single flexible design DEMET unit. For simplicity of graphic and tabular presentation, only one of the alternative advanced procedures is shown, it is labeled "special". Spent FCC catalyst was demetallized in the laboratory pilot plant. Microactivity and XRD testing were performed in accordance with ASTM standards. Steaming was performed at 1450°F 100% steam for 4 hours and 16 hours. The results prior to steaming and after 4 and 16 hours of steaming are shown in the Table 3 in comparison of the fresh, spent, standard demetallized, and special demetallized sample performance demonstrated by MAT testing.

Table 2. Fresh, Spent, and Demetallized Spent FCC Catalyst Solid and Leachate Analyses (ppm)

Elements Analyses by ICP	UTS LDRII TCLP	Fresh Catalyst			Spent Catalyst			Demetallized Spent			Element removal w% _{spent}
		Solid		Leachates	Solid		Leachates	Solid		Leachates	
		TCLP	DIF		TCLP	DIF		TCLP	DIF		
Aluminum	142110	87.469	0.549	141190	114.813	2.961	175200	34.010	4.720	+24%
Antimony	2.1	246	bdl	bdl	1526	1.766	9.491	310	bdl	bdl	80%
Arsenic	5.0	215	0.223	bdl	250	1.495	bdl	96	0.113	0.205	62%
Barium	7.6	118	0.018	bdl	77	0.667	0.014	52	0.329	0.060	32%
Beryllium	0.014	3	0.006	0.002	38	0.368	0.509	10	bdl	0.014	74%
Bismuth	bdl	bdl	bdl	7	0.319	0.015	bdl	bdl	bdl	bdl
Boron	20	0.029	0.021	20	0.109	0.094	14	0.067	0.037	30%
Cadmium	0.19	4	bdl	bdl	20	bdl	bdl	30	bdl	bdl	-55%
Calcium	1372	7.059	0.278	1819	1.889	0.283	961	4.061	1.084	47%
Cerium	4682	13.183	0.085	1171	14.915	0.065	1264	26.627	3.481	+ 8%
Chromium	0.86	675	0.043	0.011	586	bdl	bdl	579	bdl	bdl	-16%
Cobalt	8	bdl	bdl	193	0.013	0.013	12	0.142	0.052	93%
Copper	9	0.013	0.009	29	0.103	0.002	9	0.012	0.001	69%
Iron	3053	0.219	0.016	4292	0.328	0.301	902	2.320	0.053	79%
Lanthanum	3518	8.401	0.017	2757	46.975	0.246	2782	57.195	8.928	+1%
Lead	0.37	27	bdl	bdl	38	bdl	bdl	bdl	bdl	bdl	-99%
Lithium	42	0.054	0.007	56	0.431	0.314	32	0.385	0.285	43%
Magnesium	316	2.041	0.106	62	0.827	0.094	33	0.844	0.333	47%
Manganese	12	0.055	0.001	12	0.052	0.001	8	0.036	0.012	33%
Mercury	0.020	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Molybdenum	8	0.016	0.011	14	0.227	0.474	4	0.058	bdl	71%
Neodymium	2303	8.914	0.036	1703	20.987	0.192	1182	31.298	3.293	31%
Nickel	5.0	33	0.049	0.006	3432	1.868	0.269	153	1.745	0.547	96%
Potassium	890	2.801	0.348	281	1.205	0.224	242	0.097	0.012	16%
Presodymium	587	1.991	bdl	432	6.347	bdl	381	9.512	1.071	11%
Selenium	0.16	11	0.046	bdl	10	0.040	bdl	bdl	bdl	bdl	-99%
Silicon	310010	68.917	8.428	310485	50.384	32.506	282500	55.571	8.440	9%
Silver	0.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Sodium	3178	62.518	12.795	2283	26.993	16.473	2211	16.367	12.147	3%
Sulfur	2973	84.625	61.931	446	1.134	0.882	2357	86.837	13.326	+428%
Thallium	0.078	92	0.047	0.032	60	0.867	0.353	bdl	bdl	bdl	-99%
Tin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Titanium	4170	0.064	0.029	7550	0.016	0.165	3800	0.264	0.016	50%
Vanadium	0.23	63	0.137	0.160	4967	48.437	68.500	1176	0.123	0.187	76%
Zinc	5.3	91	0.537	nt	136	0.162	bdl	95	1.360	0.098	30%
Analyses											
by XRF		solids only			solids only			solids only			
Bromine	< 0.4			< 0.4			< 0.4			NoChange
Cesium	< 7.5			22.3< 7.5			22.3< 7.5			NoChange
Gallium	28.6+/- 1.0			53.2+/- 2.0			29.7+/- 2.0			44%
Germanium	< 0.7			2.1+/- 0.5			< 1.0			-99%
Indium	< 0.6			< 1.8			< 1.8			NoChange
Iodine	9.4+/- 2.8			22.5+/- 4.0			10.3+/- 3.0			54%
Niobium	13.7+/- 1.0			25.3+/- 1.0			9.9+/- 0.8			61%
Phosphorus	653.0+/-38.0			666.0+/-37.0			604.0+/-31.0			9%
Rubidium	3.6+/- 0.5			2.9+/- 0.6			1.7+/- 0.6			41%
Strontium	60.5+/- 1.0			67.5+/- 1.0			60.6< 1.4			10%
Tantalum	< 4.9			< 8.0			< 8.0			NoChange
Tellurium	< 1.4			< 2.5			< 2.5			NoChange
Thorium	6.7+/- 1.0			18.7< 1.0			16.8+/- 1.0			10%
Tungsten	<3.1			< 18.9			< 18.9			NoChange
Uranium	2.7+/-1.0			4.1+/- 1.1			3.2+/- 1.1			22%
Yttrium	59.8+/-1.0			32.6+/- 1.0			27.4+/-1.0			15%
Zirconium	103.0+/-1.0			125.0+/- 2.0			125.0+/- 2.0			NoChange

Note: bdl = below detection limit; nt=not tested; ~99%=removal to below detection limits.

Table 3. Fresh, Spent, Standard Demetallized, and Special Demetallized Spent Catalyst

	Fresh without DEMET	ECAT without DEMET	DCAT after Standard DEMET	DCAT after Special DEMET
<u>MAT yields prior steaming, wt%</u>				
Conversion	94.29	55.55	67.74	70.78
2nd Order Conversion	16.50	1.25	2.10	2.42
Gasoline/Conversion	0.27	0.63	0.56	0.54
2ndOrderConversion/Coke	0.79	0.15	0.24	0.21
Dry Gas/2ndOrderConversion	0.38	1.55	1.23	1.03
LCO/LCO+Slurry	0.47	0.52	0.60	0.63
Hydrogen	0.29	0.46	0.26	0.46
Dry Gas (C1+C2s)	6.22	1.93	2.57	2.50
Propane	17.06	0.85	2.30	1.74
Propylene	2.17	2.74	4.34	4.84
Isobutane	14.36	2.28	6.17	5.60
Normal_Butane	6.65	0.56	1.35	1.22
Isobutene	0.39	0.93	0.96	1.17
Total Butenes	1.21	3.24	3.91	4.51
Gasoline (C5-430F)	25.41	34.98	38.10	38.34
LCO (430-650F)	2.66	22.94	19.36	18.55
Slurry (650F+)	3.05	21.51	12.91	10.68
Coke	20.91	8.51	8.74	11.56
<u>MAT yields after 16 hours steaming, wt%</u>				
Conversion	62.91	35.86	40.38	56.56
2nd Order Conversion	1.70	0.56	0.68	1.30
Gasoline/Conversion	0.66	0.56	0.65	0.68
2ndOrderConversion/Coke	0.37	0.07	0.14	0.45
DryGas/2ndOrderConversion	1.11	2.98	2.55	1.37
LCO/LCO+Slurry	0.68	0.33	0.37	0.52
Hydrogen	0.07	0.64	0.34	0.21
DryGas (C1+C2s)	1.88	1.67	1.72	1.78
Propane	1.19	1.01	0.66	0.79
Propylene	4.22	1.73	2.21	3.97
Isobutane	3.94	0.54	0.95	2.54
Normal_Butane	0.82	0.19	0.28	0.51
Isobutene	1.17	0.63	1.19	1.99
Total Butenes	4.77	1.63	3.17	5.70
Gasoline (C5-430F)	41.47	20.18	26.22	38.20
LCO (430-650F)	21.36	20.89	21.92	22.47
Slurry (650F+)	15.73	43.25	37.70	20.98
Coke	4.56	8.28	4.83	2.87

Demetallized spent FCCU catalyst TCLP leachate is below the proposed LDR-II UTS for all 14 elements.

Demetallization for primary recycling to FCCUs can reduce fresh catalyst additions, reduce circulating inventory metals (or hold a metals level with increasing feed stock metals), and reduce leachable metals for a portion of spent catalyst withdrawn. Contaminant metals are controlled in FCCUs due to their deleterious affects on conversion, selectivity, and deactivation of fresh catalyst. Similarly, cement kiln blends are limited to a kiln blend of 83 ppm vanadium due to potential problems with refractories (Petrovsky, 1994). For those kilns not already at a vanadium limit due to vanadium content of the local quarry supply, the dilution of vanadium sets the limit of spent FCCU catalyst processed to 1-2% of kiln feed stock. The mobility of vanadium is well known in refining, and it appears the conditions of cement kiln processing do not limit vanadium mobility. Demetallization could be used to reduce the leachable metals prior to secondary recycling (cement kilns, etc.) or disposal. Using DEMET to remove vanadium from feed stocks to cement kilns would increase capability to substitute spent FCCU catalyst in the kiln blend." (Pavel, 1995)

Conclusion. Demetallization reduces the leachability of contaminant elements measured by TCLP and de-ionized water flushes. After demetallization of spent FCCU catalyst all fourteen TCLP leachate elements are below the proposed LDR-II Universal Treatment Standard levels. For every indicator of catalyst performance after severe steaming, standard demetallization appears superior to equilibrium catalyst without demetallization, and special demetallization appears superior to standard demetallization and far superior to equilibrium catalyst without demetallization. Graphs show higher conversion, and higher gasoline yields with lower coke for special demetallized catalyst compared to equilibrium catalyst. The graphs also show the special demetallized catalyst performance ratios are also superior with lower dry gas/kinetic conversion ratios, higher gasoline/coke ratios, higher gasoline/conversion selectivities, higher light cycle oil selectivities, higher dynamic activities, as well as increased C3 and C4 olefins and isobutylene. DEMETallization appears very well suited for the marketplace of new gasolines and higher middle distillate demands. The special DEMET process significantly increases the activity, selectivity and hydrothermal stability of the catalyst and minimizes the fresh catalyst required to maintain FCCU activity.

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DETERMINATION OF TOTAL MERCURY IN COAL

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INTRODUCTION

The determination of mercury in coal is of interest due to its extreme volatility during coal combustion and its potential to be toxic if released into the environment. However, the low concentration of mercury in coal, frequently at the low ng/g level, makes analysis extremely difficult. In addition, mercury's volatility makes sample cross-contamination more likely. Despite the emphasis placed on mercury analysis, the analytical method of choice to give accurate, reproducible results for coal samples remains debatable. In 1988, 18 independent laboratories participated in an interlaboratory comparison of EPA Method 245.5 (sample digestion/dissolution followed by amalgamation/CVAA) for the analysis of mercury in NIST-SRM 1633a coal fly ash which has a certified value of 0.16 ± 0.01 $\mu\text{g/g}$. The results gave a mean that was 230% of the true value with an overall standard deviation of 200%.¹ More recently, an extensive round robin experiment on Hg analysis was carried out in which 11 laboratories were supplied with three different coals for analysis. The analytical methods employed were cold vapor atomic absorption spectroscopy (CVAAS), cold vapor atomic fluorescence spectroscopy (CVAFS), and instrumental neutron activation analysis (INAA). The study showed that there was approximately a 50% inter-laboratory variability corresponding to a reproducibility of 0.04 $\mu\text{g/g}$ for a coal with an approximate Hg concentration of 0.08 $\mu\text{g/g}$.²

INAA is one method that has commonly been used for mercury analysis in coal. NAA has the advantage over other analytical methods in that once the sample is sealed in the irradiation vial sample cross-contamination is prevented. However, the ^{75}Se ($t_{1/2}=120$ d) 279.5 keV γ -ray is a direct spectral interferant for the ^{203}Hg ($t_{1/2}=47$ d) 279.2 keV γ -ray. The interference can be mathematically corrected for using the ^{75}Se 264.7 keV γ -ray, but this can result in large uncertainties associated with the mercury values, particularly in coal samples where the selenium concentration is many times larger than the mercury concentration.

Our laboratory has developed a new radiochemical neutron activation analysis (RNAA) method based on pyrolysis followed by double gold amalgamation. During pyrolysis the more volatile elements, such as mercury and selenium, are liberated from the coal sample, and the mercury is preferentially collected by amalgamation with gold. While this procedure does not completely separate the mercury from the selenium it does greatly increase the Hg-to-Se ratio in the 279 keV peak, thereby reducing the measurement's uncertainty. Furthermore, since other elements in the sample are not amalgamated with the gold, the spectrum background is drastically reduced which results in a greater sensitivity for mercury.

EXPERIMENTAL

Sample Preparation

Samples of NIST SRM 1632a were dried at 105°C overnight and cooled. 10.00 $\mu\text{g/mL}$ and 50.00 $\mu\text{g/mL}$ Hg solutions were prepared from a 1000 ± 3 $\mu\text{g/mL}$ Hg in 2% HNO_3 certified standard (High Purity Standards). Appropriate amounts were added to

known quantities of dry SRM 1632a to obtain spike concentrations of approximately 200, 400, 650, and 1000 ng/g. The spiked samples were dried at 35-45°C overnight. After cooling, the samples were shaken on a mixer mill for twenty, 2-3 minute intervals.

Irradiation

Approximately 70-100 mg of the spiked standards were placed in acid washed quartz vials (4 mm i.d., 6 mm o.d.) and sealed. Samples were irradiated at the University of Missouri Research Reactor (MURR) for 48 hours at a thermal flux of 5.150×10^{13} n/cm²/sec. One to two weeks after irradiation the vials were washed with aqua regia.

Radiochemical Separations

Apparatus. The experimental setup is shown in Figure 1. All glassware was constructed of quartz and was soaked overnight in 10% HNO₃ prior to analysis. Quartz wool was placed in the tube furnace downstream from the sample to trap coal particulates and ensure complete pyrolysis.

Gold traps were prepared by folding a 10 cm x 10 cm gold mesh in half and rolling lengthwise. These gold mesh "cylinders" were blanked by heating to 800°C for 1 hour. After cooling, each mesh was placed inside a 6 mm i.d. quartz tube with quartz wool plugs at each end to keep the mesh in place.

Procedure. Sample vials were cooled in liquid nitrogen for several minutes, wrapped in a thin layer of quartz wool, and rolled in aluminum foil. The vials were crushed and the foil was partially unwrapped before being placed inside the tube furnace. Samples were then heated to 550°C for 1 hour. After the furnace had cooled to <90°C, the heating tape wrapped around the first gold mesh was heated to 400°C for 30 minutes. Throughout the procedure the nitrogen flow rate was kept constant at about 250 mL/min.

Counting

Activated samples were counted prior to being opened (as in INAA) for 6 hours with a HPGe detector. After radiochemical separation the second amalgamated gold mesh was counted for 4 hours with a larger, higher efficiency HPGe detector.

RESULTS & DISCUSSION

Typical γ -ray spectra obtain before and after radiochemical separation are shown in Figures 2 & 3. The reduction in the spectral background results in a lowering of the sensitivity for mercury from about 190 ng/g for INAA to about 15 ng/g for RNAA (calculated using the $3\sigma_{\text{BKG}}$ method).

The radiochemical separation also greatly reduces the uncertainty associated with a mercury determination due to the increase in the Hg-to-Se ratio in the 279 keV peak. Prior to separation, the relative standard deviation (rsd) in the specific activities (counts in the 279 keV peak per gram of sample) ranged from 12% for the 1000 ng/g spiked sample to 75% for the 200 ng/g spike sample. After separation, the rsd of the specific activities ranged from 1-4%.

The accuracy of the method was evaluated with SRM 1632a. RNAA analysis yielded an experimental value of 114 ± 13 ng/g, well within the certified Hg concentration of 130 ± 30 ng/g. Although only one sample of the standard has been analyzed thus far the results are very promising, and repeat analyses of the SRM are planned in the future.

The linearity and reproducibility for the method are illustrated in Figure 4. The correlation coefficient for these results was calculated to be 0.916 suggesting reasonable linearity. The discrepancy seen in the reproducibility is most

likely introduced during the opening of the vials. It is possible that some sample was lost during the breaking of the vial and/or placement in the tube furnace.

SUMMARY

As increasing emphasis is placed on sensitive and accurate mercury determinations, analytical methods will be placed under more scrutiny and current methods have already been shown to yield inconsistent results. To meet future requirements, either current methods must be revised or new methods must be developed.

In the development of this analytical method the greatest obstacle encountered thus far has been devising a process that ensures quantitative sample recovery during vial opening. The focus of future research will be on refining this aspect of the procedure.

Despite this difficulty, performing radiochemical separations using pyrolysis and amalgamation on irradiated coal yielded accurate results and resulted in significant improvements in sensitivity and the relative standard deviation in mercury determinations. Both of these characteristics are critical in yielding reliable, accurate results for the analysis of mercury in coal.

ACKNOWLEDGMENTS

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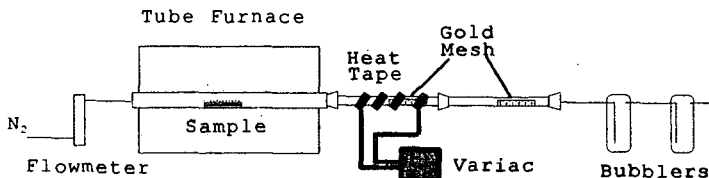


Figure 1. A schematic of the experimental setup for the radiochemical separation of mercury.

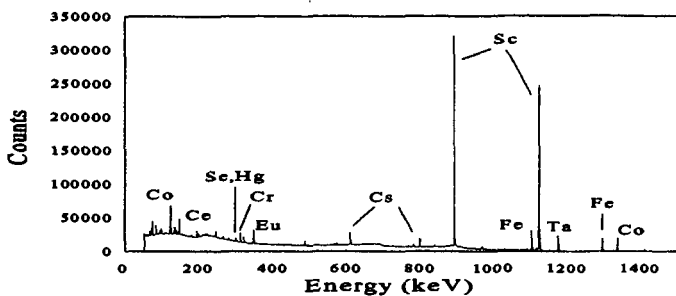


Figure 2. γ -ray spectra of irradiated coal. (48 hour irradiation, 80 day decay, 6 hour count).

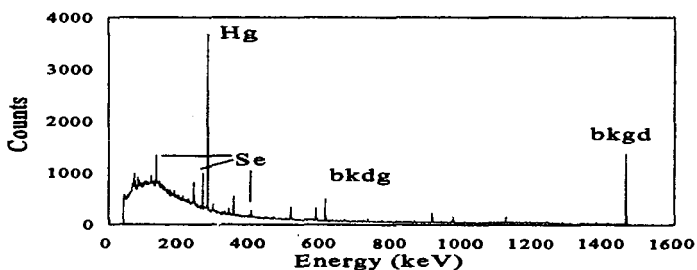


Figure 3. γ -ray spectra of amalgamated gold containing mercury from coal sample. (75 day decay, 4 hour count).

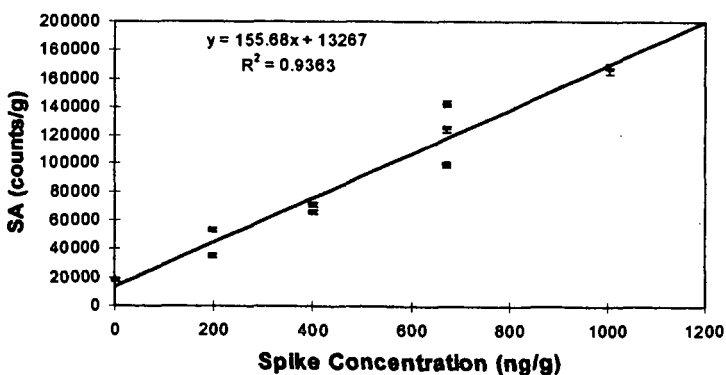


Figure 4. Graph of specific activity vs. Spike concentration.

EVALUATION OF MICROWAVE DIGESTION AS THE PREPARATION METHOD FOR MERCURY-IN-COAL MEASUREMENT

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Keywords: Microwave digestion, mercury in coal, mercury analyzer

INTRODUCTION

The 1990 Clean Air Act Amendment (CAAA) empowered the U.S. Environmental Protection Agency (EPA) to set emission standards for a number of potentially hazardous air pollutants (HAPs) generated by a variety of specific combustion sources. Eleven elements (or compounds of these elements) present in coal are among the 189 pollutants identified as air toxics by the CAAA legislation. Mercury is included in this list. Generally mercury concentrations in coal are well below 1 ppm (1 $\mu\text{g/g}$). However, because such a large tonnage of coal is consumed for electric power generation, coal combustion represents a potentially significant source of mercury entering the environment (1).

Determination of the concentration of mercury in coal is becoming an increasingly important issue. Because of the relatively low concentration of mercury in coal and the relatively high detection limits of current analytical methods, information on the mercury content of coals to any degree of certainty is still unavailable. Therefore, evaluating the precision and accuracy of current analytical methods and improving existing methods are very important in estimating potential atmospheric emissions and associated risks.

Complete sample dissolution is necessary prior to instrumental analysis for most solid samples. In general, this step is the most critical in trace metal analysis and is time-consuming and labor-intensive. Several preparation methods are currently being used for mercury-in-coal measurements. A method (2) that combusts the coal sample in a tube furnace and collects the mercury vapor using a gold wire collector has shown some higher results (1) compared to other methods. Method ASTM D3684 uses an applied oxygen combustion bomb on the coal sample and subsequent rinsing of the inside of the bomb after combustion. Method SW846 is an open-beaker acid digestion method, which has been considered not suitable for mercury determination because of the volatile properties of mercury. The method presented here has proven to be reliable and rapid for the decomposition of coal samples for mercury determination, as well as for other trace metals.

EXPERIMENTAL

Instrumentation

A Model MDS-2100 microwave oven (CEM Corporation) with pressure control was used. The power range (maximum 950 W) of the oven was adjusted to 1% increments. Since the sample decomposition consists of several separate stages of control, the microwave is also equipped with a removable 12-position carousel. Teflon vessels of 100-mL volume, allowing a maximum 120 psi of pressure, were used.

A Leeman Labs, Inc., PS200 automated mercury analyzer was used as the analytical instrument to measure the mercury in digested coal acid solutions. The pump rate was 5 mL/min. The gas flow rate was 0.3 L/min.

Reagents and Standards

Concentrated sulfuric acid, concentrated nitric acid, and concentrated hydrochloric acid were all trace metal grade. SnCl_2 and $\text{Mg}(\text{ClO}_4)_2$ were analytical grade. Mercury standards were analytical grade.

Procedures

Microwave Digestion

Approximately 0.5 g of coal, accurately weighed to 0.0001 g, was placed in a Teflon microwave digestion vessel with 1 mL of concentrated sulfuric acid and 0.25 mL of concentrated nitric acid (added separately). Approximately 2 minutes was given for the reaction to take place. An additional 1 mL of concentrated nitric acid was then added to the vessel. The digestion vessels were capped and placed

in the microwave, and Step 1 was run (See Table 1). The vessels were removed from the microwave after the run was completed. The vessels were cooled to room temperature and the gases vented. An additional 2 mL of concentrated nitric acid was added to the vessel. The digestion vessels were put through additional heating (Steps 2 and 3) until the solution was a clear light yellow color, with cooling and venting between each step. 0.5 mL of concentrated hydrochloric acid was put in each digestion vessel, and Step 4 was run. 5 mL of concentrated hydrochloric acid was added, and the solution was diluted to 50.0 mL with distilled water in a volumetric flask. The solution was filtered and run on the cold-vapor atomic adsorbance (CVAA) mercury analyzer using matrix-matched standards.

Cold-Vapor Atomic Absorption Mercury Analyzer

After about 1 hour equilibrating the instrument, a five-point calibration was performed. A quality control standard was analyzed immediately after the instrument was standardized to verify calibration accuracy. Samples were run in duplicate, with the mean reported. A calibration check standard was analyzed every ten samples. If the check standards did not read within 10% of the expected value, the instrument was recalibrated. A sample spike was performed every ten samples as well as for each different matrix to verify analyte recovery. A digestion blank and one standard reference material was run along with the samples for quality assurance.

RESULTS AND DISCUSSION

Effect of Acids in Combination

Hot concentrated perchloric acid is a strong oxidizing agent that attacks metals that are unresponsive to other acids. However, hot concentrated perchloric acid is potentially explosive when in contact with organic material (3). Because of this potential hazard, alternative acids to complete dissolution were investigated, and perchloric acid was not used.

Sulfuric acid is a highly effective solvent for many organic samples. Hot concentrated sulfuric acid can completely destroy almost all organic compounds. In this study, sulfuric acid was added as the first step to convert the organic compounds in the coal to inorganic carbon. Because sulfuric acid absorbs the water generated during the reaction, the equilibrium is pushed to the right, helping to maintain the reaction.

Nitric acid is a strong oxidizing reagent widely used for liberating trace metals from various types of matrices as highly soluble nitrate salts. Nitric acid added after the sulfuric acid will convert inorganic carbon to carbon dioxide and produce soluble salts. But only a small amount (0.25–0.5 mL) of nitric acid should be added at first to allow the reaction to start at ambient temperature. If 3 mL of total nitric acid was added at one time, the reaction between the coal and acids would actually slow down as a result of the large amount of water in the concentrated nitric acid (more than 30%) absorbing the heat.

Hydrochloric acid is used for dissolution of coal and, more importantly, for preserving mercury in solution.

Bloom (4) and other researchers (5) reported that most trace metals, including mercury, are completely leached from silicate and sulfide minerals by hot acids; thus there is no need for complete hydrofluoric acid breakdown. Trials using hydrofluoric acid at the end of the digestion stage were carried out in this investigation. The analysis results showed no difference. Therefore, hydrofluoric acid was not used in the digestions.

A comparison was made of digestions with and without sulfuric acid. The results showed a 50% longer digestion time for complete dissolution without sulfuric acid. Adding a mixture of the acids to the coal sample instead of adding them separately was tested. Longer digestion times and incomplete digestions resulted in poor precision and accuracy.

Efficiency of Digestion

Although many studies have been devoted to evaluate recoveries of trace metals from coal matrices, little has been done to establish how completely the coal was digested. If a clear and colorless solution resulted, it has been assumed that digestion was complete. A visible residue of silicate material (a grayish color) often remained. In the case of high-ash coals, the presence of this residue made confirmation of complete digestion even harder. Matusiewicz et al. (5) used total residual carbon to evaluate the degree of completion of digestion. This digestion method was used in several interlaboratory proficiency studies and round-robin studies for mercury and other trace metals, and the overall results indicate that this digestion method is precise and accurate.

Pressure Evaluation

The pressure of the first stage was set at 40 psi, and the power was set with slow ramp. The running time should be adequate to allow the sulfuric acid to react with the coal completely. The maximum pressure in the second stage was raised to 70 psi, because after additional nitric acid is added, the reaction between inorganic carbon and nitric acid can be very violent and large amounts of gases can be generated, resulting in a rapid pressure increase and membrane blowout. The pressure control was connected to the vessel containing the largest and, presumably, the most reactive sample when different types of samples were digested at the same time. Different types (i.e., different ranks) of coal have different responses to microwave pressure. Low-rank coal tends to be digested fairly easily because of its loose organic structure and low carbon content. High pressure is generated in the first couple of steps as a result of the rapid chemical reaction. A low percentage of microwave power should be applied to such samples.

Potential Sources of Interference and Contamination

Organic matrices cause interference on inorganic instrumentation. Some researchers used postdigestion methods such as a potassium persulfate digestion after the microwave digestion to reduce the organic matrices. But we found the method presented here provides a good, complete digestion with good precision and accuracy without any postdigestion. Also, postdigestion can potentially become a source for contamination.

Matrix-matched standards were used to compensate for any contamination from the trace-metal-grade acids used.

The mineral content in coal gave very small or no interference on instrument readings because of the very small amount of mineral content left after the complete digestion.

A digestion blank is very important for accurate analyses of the trace level of analytes in most fossil fuel samples. As impurities in the acids used are compensated for using matrix-matched standards, the digestion blank will verify other potential sources of contamination occurring during the digestion period.

Precision and Accuracy

Without any other laboratory's involvement for testing the method, we cannot verify this method's precision and accuracy, but we can discuss the data we generated from the perspective of precision and accuracy. Tables 2 and 3 show the instrumental precision and digestion precision and accuracy for the three standard reference materials used in this investigation.

A relatively large sample size, about 0.5 g compared with most other methods using 0.1–0.2 g, gives more analyte in the solution provided, resulting in a more accurate reading, since mercury in most of the coals are at trace levels and are barely above the instrument detection limit after the dissolution.

Instrument Detection Limit

The instrument detection limit for coal matrices was calculated based on the seven readings of several different low-level mercury matrix-matched standard concentrations (between 0.1 and 0.5 ppb). The method used for calculation was Code of Federal Regulations 40. The detection limit for coal on the instrument used in this study is 0.1 $\mu\text{g/L}$ in digestion solution or 0.01 $\mu\text{g/g}$ in solid, based on 0.5 g of coal digested and brought to a final volume of 50 mL.

CONCLUSION

Sample digestion in pressurized Teflon vessels using microwave heating proved to be a very rapid method for the complete digestion of fossil fuel samples. Results obtained from this study for trace mercury in coal are in good agreement with certified values. The use of HClO_4 at high temperature and high pressure should be avoided because of the potentially explosive nature of the acid. Multiple digestions and analysis for other important trace metals in a certified standard reference material (National Institute of Standards and Technology) [NIST] 1635 and South Africa Reference Material [SARM] 19 were carried out by the Analytical Research Laboratory investigators at the Energy & Environmental Research Center. Data showed that this digestion method is a good coal dissolution method for other trace metals (As, Cd, Ni, Se, Cr, Be, etc.) in coal.

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TABLE 1

The Microwave Setup								
Coal Digestion Step 1					Coal Digestion Step 2			
Stage	1	2	3	4	Stage	1	2	3
Power	25	35	40	40	Power	40	45	50
PSI	30	40	45	50	PSI	30	40	60
Time (min)	10	10	60	60	Time (min)	10	10	30
TAP (min)	1	1	60	60	TAP (min)	1	1	30
Fan	100	100	100	100	Fan	100	100	100

Coal Digestion Step 3				Coal Digestion Step 4			
Stage	1	2	3	Stage	1	2	3
Power	30	50	60	Power	35	50	60
PSI	60	85	100	PSI	80	90	100
Time (min)	10	10	20	Time (min)	10	10	20
TAP (min)	1	1	20	TAP (min)	1	1	20
Fan	100	100	100	Fan	100	100	100

TABLE 2

Instrumental Precision			
	1635	SARM 19	SARM 18
% RSD *	2.40	2.45	2.43

* % relative standard deviation (RSD) was from seven readings.

TABLE 3

Digestion Precision and Accuracy						
	SARM	NIST	SARM 18	Commanche	Absaloka	Blacksville
Uncertified Value	0.2	0.02	0.04	NA*	NA	NA
EERC Result	0.207	0.0186	0.024	0.071	0.049	0.084
% RSD**	11.9	32.8	2.56	8.2	19.0	23.9
Number of Digestions	14	12	8	NA	NA	NA
% Recovery	104	93	60	NA	NA	NA

* Not applicable.

** % RSD was calculated from number of digestions.

PRECOMBUSTION REMOVAL OF MERCURY FROM COAL BY MILD PYROLYSIS

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Keywords: mercury in coal, mild pyrolysis, clean coal

INTRODUCTION

Coal combustion is one of the most popular sources for energy in the United States. However, increasing environmental regulations concerning the emissions of various pollutants resulting from coal combustion are being promulgated. Title III of the 1990 Clean Air Act Amendments specifies that air toxics will be controlled to the maximum extent technically possible (maximum available control technology, MACT). A number of compounds listed as toxic are found in coal and are released into the atmosphere when coal is burned. Under Title III, a plant that emits over 10 tons/year of any one of the listed toxic compounds, or emits over 25 tons/year (or more) of any combination of these pollutants are required to comply to the control standards. Mercury is present in coal at varying ppm ($\mu\text{g/g}$) levels and is considered to pose a significant environmental health risk from coal combustion. Reviews¹ on mercury in the ambient air have suggested that the average concentration of mercury in the gaseous form in regionally polluted areas, such as the east coast, are in the range between 3 to 4 ng Hg/m³. And in urban air the average concentrations may be as high as 10 ng Hg/m³. Coal combustion has been estimated to account for over 8 % of the mercury emissions to the atmosphere.² Lindberg³ reported that in the plume of a coal-fired power plant, gaseous mercury is present in excess of 1000 ng Hg/m³ within a few kilometers of the source. Material balances on mercury in power plants have shown that only approximately 10% of the total mercury from the coal is found in the fly ash, and the remainder exits the stack in vapor form.^{4,5} Other studies investigating the effects of existing flue gas clean-up (FGC) technologies on mercury concentration in flue gases report that varying levels of removal can be achieved, ranging from 10% to 90% removal.^{6,7,8,9} This large variation is most likely due to differences in combustion reactors as well as differences in the chemical form of mercury and variations in chlorine levels in the feed coal.

The terminology of pyrolysis is used to refer to the processes in which coal is heated in the absence of oxygen. The coal partially decomposes and produces gaseous, liquid and solid residuals. Mild pyrolysis is performed using low temperatures ($<600^{\circ}\text{C}$), low pressure (about 1 atm.) and usually low heating rates. The original coal matrix remains largely intact while the heating value of the coal is retained. Mild pyrolysis of coal has been shown to be an economically and technically viable method of desulfurization and denitrification.^{10,11} Most "organic" sulfur in Ohio #8 coal is released below 500°C in the form of H_2S which can be quickly scrubbed by solid sorbents. During pyrolysis the majority of trace elements in coal are retained in the solid residue, but volatile elements such as mercury, bromine, and antimony are released in vapor form. Elemental mercury has a low boiling point (356°C) and has been shown to be released from coals at the lower temperatures indicative of mild pyrolysis.^{12,13,14} The release of mercury from the coal structure before combustion by mild pyrolysis offers the greatest potential for the separation of mercury and its compounds from the evolved gases and vapors. The concentration of these species are at their greatest in the vapor phase during this period and may be collected by means of adsorption or chemisorption to solid sorbents. This precombustion removal represents a pollution prevention strategy. (Regulations controlling the release of mercury will most likely be promulgated in the future for coal burning power plants.)

This study investigates the influences of temperature and residence time on the evolution of mercury from coal during mild pyrolysis. While optimizing the temperature and residence time so as to maximize the evolution of mercury, it was also important to maintain the original heating value of the parent coal.

MILD PYROLYSIS METHODOLOGY

A Lower Freeport #6A coal mined in Harrison County, Ohio was the primary coal investigated in this study. The Lower Freeport sample was sieved to 115 x 150 mesh ($\sim 115\mu\text{m}$) size prior to shipment. During the sieving and shipment time period the sample lost some moisture and became slightly oxidized. The condition of the sample as received was maintained by storing it with CO_2 headspace in poly-urethane containers. A Pittsburgh #8 Coal mined in Greene County, Pennsylvania was also used in this study so as to provide a comparison. This sample was also sieved to 115 x 150 mesh ($\sim 115\mu\text{m}$) size and was maintained in an as received condition by storing it with CO_2 headspace in poly-urethane containers. The two parent coal samples examined in this study are high volatile bituminous coals. The original samples were riffled for characterization tests, and a summary of the test results is shown in Table I.

The mild pyrolysis process was carried out in a Lindberg tube furnace with nitrogen flow. A diagram of this system is shown in Figure 1. It is a well known fact that trace values for mercury in coal vary largely even within a single coal seam. Before pyrolyzing the coal samples, it was necessary to extract a portion of the coal (~10grams), cone and separate that portion so as to produce a homogenized sample, and then determine a mean value for the mercury content of that homogenized sample. Samples to be pyrolyzed were then extracted from the homogenized sample, weighed to $0.5g \pm 0.1mg$, and placed in nickel alloy sample boats. The tube furnace was stabilized at a predetermined temperature, and the nitrogen flow was regulated so that the gas velocity in the hot zone of the tube was maintained at approximately 3cm/s.

Each sample was placed in the cool zone of the tube and purged of any trapped gases by the nitrogen flow. The sample was then pulled into the hot zone of the tube furnace and heated for a predetermined time. The sample was then pushed back into the cool zone of the tube where it remained in a nitrogen atmosphere until room temperature was achieved. The pyrolyzed coal was then analyzed for total mercury content using the ASTM D3684-78 procedure. The ASTM method was written specifically for fresh coal samples, but should effectively mineralize the pyrolyzed coal as well.

EXPERIMENTAL RESULTS AND DISCUSSION

Coal samples were subjected to mild pyrolysis conditions and percent removal of mercury was determined by comparing the final total mercury content of each pyrolyzed sample with an initial mercury value. The initial mercury value for each sample was calculated by multiplying the weight of the sample prior to pyrolysis with the mean mercury value which was established for the homogenized coal from which the sample was extracted.

The results are shown in Table 2, and graphical representations of the mercury removal as a function of temperature are shown in Figures 2 and 3. The data indicate a general trend within each residence time data set in which the percent removal increases with temperature rise, peaks at some temperature, and then declines. Thermomechanical analysis of both parent coals revealed that the two coals become fluid at about 400°C and remain fluid until resolidification occurs at 464°C for the Lower Freeport sample and 477°C for the Pittsburgh coal sample. When a coal is heated at temperatures in which it becomes plastic, a soft layer develops on the outside of the coal particles and internal depolymerization occurs. As the carbon becomes soft, it swells and traps gases. Once the coal becomes more plastic, the gases break through. It is possible that once the coal becomes plastic, the evolution of the mercury is greatly inhibited by this trapping action. The increased heating rate accompanying the higher temperatures increases the trapping because the devolatilization is greater than the plasticity.

Within each temperature range data set, a general trend exists in which the removal of mercury initially increases rapidly with residence time and then levels off as it seemingly approaches an asymptotic limit. This suggests that under the conditions given in the methodology, the rate of evolution of total mercury is proportional to the fraction of mercury and its compounds remaining in the char at any time multiplied by some reaction rate coefficient dependent on temperature. This can be expressed as a first order homogeneous decomposition with an asymptote dependent on temperature, time, reactor configuration, pressure, heating rate, and particle size:

$$\frac{X}{X_{\max}} = 1 - e^{-kt}$$

Where: X = percent conversion

X_{\max} = maximum percent available for conversion under a specified set of conditions

t = reaction time (min)

k = reaction rate coefficient (min^{-1})

By maximizing the regression coefficient when comparing the experimental data to the linear form of the equation, X_{\max} can be obtained for each temperature. The slope of the linearization provides a value for k , the reaction rate coefficient. Table 3 lists the values of X_{\max} with the corresponding R^2 and k for both coal samples and all temperatures. A comparison of the Lower Freeport #6A data with the above equation indicates a reasonable agreement between theory and measurements for all temperatures except 275°C and 325°C. The Lower Freeport #6A data indicates an interesting trend once a pyrolysis temperature of 325°C is achieved. Below this temperature, analysis results in a maximum possible removal of 100%, but after 325°C, X_{\max} increases with temperature until it peaks at 500 °C. A comparison of the Pittsburgh #8 data with the equation, however, indicates a reasonable agreement between theory and measurements only within the temperature range of 325°C to 400°C.

By applying Arrhenius' law to the Lower Freeport #6A experimental data, a plot of $\ln(k)$ vs. $1/T$ results in figure 4. The plot shows two regimes for mercury removal in the Lower Freeport #6A coal. The data produces a straight line with a large slope in the 275°C to 400°C temperature range. This indicates a large activation energy, E , which can be associated with

chemical reaction control. The temperature at which the plot's slope changes dramatically, indicating a shift in controlling mechanism of the reaction, coincides with the coal's plastic zone. Application of Arrhenius' law to the Pittsburgh #8 experimental data results in figure 5. The plot indicates that the Pittsburgh #8 coal behaves similar to the Lower Freeport #6A coal under the pyrolysis conditions given in the methodology. The activation energies for the mercury removal in the lower temperature region ($<400^{\circ}\text{C}$) are calculated using information from the equation of the straight line plotted in that temperature region. The activation energies for mercury removal from the Lower Freeport #6A coal and the Pittsburgh #8 coal are 6615 cal/gmol and 4939 cal/gmol respectively.

After treating a coal by mild pyrolysis, it is important to examine what effects the pyrolysis process has had on the overall heating value of the coal. An oxygen bomb calorimeter was used to determine the net heat of combustion of each of the Lower Freeport #6A pyrolyzed samples. These values were compared to an initial heat of combustion value which was calculated using the initial sample weight and a mean value for the net heat of combustion of the parent Lower Freeport #6A coal. Figure 6 shows a plot of this comparison. The results indicate that there is little change in the overall heating value of the Lower Freeport #6A pyrolyzed coal until pyrolysis temperatures are greater than 400°C . During the $200\text{--}400^{\circ}\text{C}$ temperature range, there is apparently little carbon loss although devolatilization of other components does occur. Once temperatures exceed 400°C , there is a decrease in overall heating value which drops with temperature rise.

CONCLUSIONS

Given the conditions of the reactor used in this study, mild pyrolysis of coal can achieve up to 74% removal of mercury from the Lower Freeport #6A coal investigated and up to 80% removal of mercury from the Pittsburgh #8 coal investigated. The results show that precombustion removal of mercury from coal by mild pyrolysis can be modeled as a homogeneous reaction with a distinct maximum percent mercury available for conversion and a distinct reaction rate coefficient for each temperature range. The results also indicate that removal of mercury occurring when pyrolysis is performed at low temperatures ($<400^{\circ}\text{C}$) on plastic or caking coals is characterized by chemical reaction control. At these low temperatures, the coal matrix suffers little destruction. The results verify that the overall heating value of the coal is essentially unaffected by mild pyrolysis at temperatures lower than 400°C .

Table I: Summary of Characterization Analysis on Original Coal Samples

	Lower Freeport #6A (Harrison Co., OH)		Pittsburgh #8 (Greene Co., PA)	
	As Determined	Dry Basis	As Determined	Dry Basis
%Ash	11.52	11.65	10.00	10.25
%Carbon	68.03	68.78	73.41	75.22
%Hydrogen	5.07	5.13	5.2	5.33
%Nitrogen	1.62	1.64	1.67	1.71
%Sulfur	4.24	4.29	1.09	1.12
%Oxygen (difference)	9.52	9.62	8.63	8.84
%Moisture	1.09 (residual)		2.40	
Density, g/cm ³		1.294		1.293
Hg Conc., ppm		0.57 ± 0.07		0.12 ± 0.04
Surface Area, m ² /g		1.105		1.386
Btu/lb	12,870	13,019	13,207	13,532
kJ/kg	29,933	30,280	30,717	31,473

Figure 1: Furnace with Nitrogen Flow

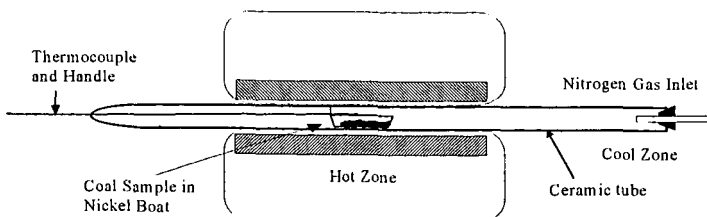


Table 2: Mild Pyrolysis Test Results

Temp. °C	Lower Freeport #6A %Removal of Mercury				Pittsburgh #8 %Removal of Mercury				
	2 Minute Residence Time	4 Minute Residence Time	8 Minute Residence Time	10 Minute Residence Time	2 Minute Residence Time	4 Minute Residence Time	6 Minute Residence Time	8 Minute Residence Time	10 Minute Residence Time
275	0	5.5	5.6	5.3	-	-	-	-	-
300	0	8.0	14.9	24.2	-	-	-	-	-
325	0	37.6	29.5	41.4	0	0	-	36.1	52.0
350	14.0	33.6	44.8	48.6	-	-	-	-	-
400	39.9	50.3	57.7	57.7	53.0	70.6	79.6	-	-
450	9.7	58.8	68.4	68.1	47.0	46.6	46.9	-	-
500	-	62.4	73.9	-	-	-	-	-	-
600	-	49.5	59.1	-	-	-	-	-	-

Figure 2: Lower Freeport #6A
Mild Pyrolysis Data

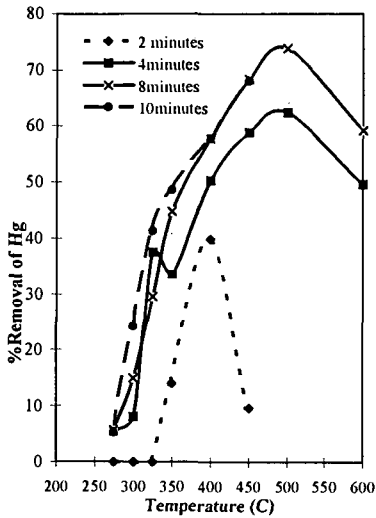


Figure 3: Pittsburgh #8
Mild Pyrolysis Data

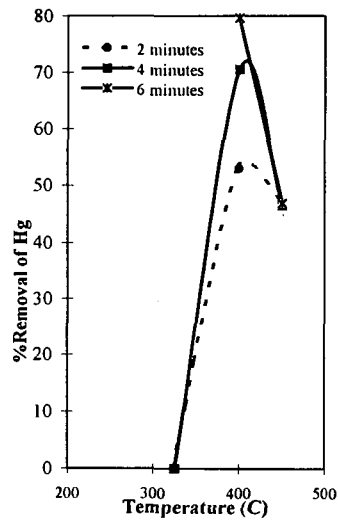


Table 3: Values of X_{max} , R^2 , and k

Temp. (°C)	Lower Freeport #6A			Pittsburgh #8		
	X_{max}	R^2	$k(\text{min}^{-1})$	X_{max}	R^2	$k(\text{min}^{-1})$
275	1.00	0.683	0.006	-	-	-
300	1.00	0.939	0.028	-	-	-
325	1.00	0.657	0.044	1.00	0.850	0.071
350	0.54	0.993	0.234	-	-	-
400	0.58	0.972	0.502	0.86	0.998	0.441
450	0.70	0.931	0.449	1.00	0.598	0.097
500	0.77	0.999	0.422	-	-	-
600	0.62	0.999	0.386	-	-	-

Figure 4: Arrhenius Plot of Lower Freeport #6A Data

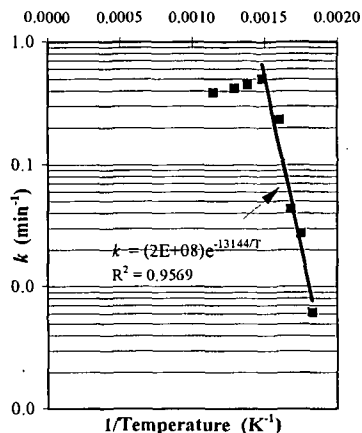


Figure 5: Arrhenius Plot of Pittsburgh #8 Data

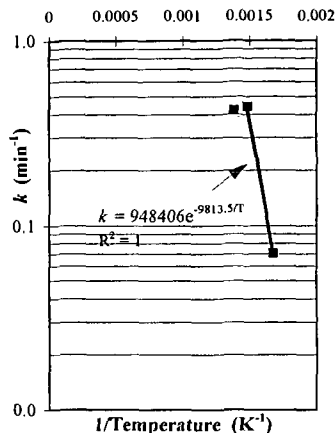
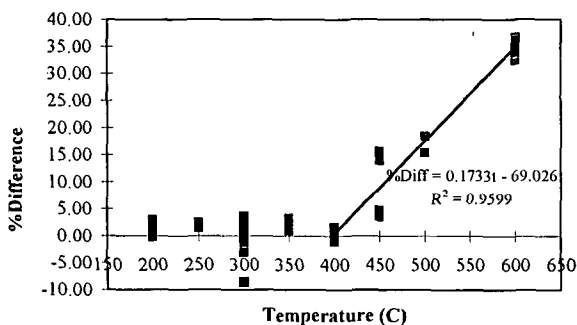


Figure 6: Comparison of Lower Freeport #6A Parent Coal and Pyrolyzed Coal Heating Values



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REACTIONS OF GASEOUS, ELEMENTAL MERCURY WITH DILUTE HALOGEN SOLUTIONS

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ABSTRACT

Of the trace elements known to exist in fossil fuels, mercury (Hg) has emerged as one of the greatest concerns. Mercury has been found to be emitted from combustion in at least two different chemical forms: elemental Hg and oxidized Hg compounds. Precise identification of the oxidized compounds emitted has not been accomplished to date. However, most workers in this field assume that mercuric chloride should be the predominant oxidized species. Mercuric chloride should be readily removed in a wet scrubber system because of its relatively high solubility in water. However, it has been presumed, and we have shown, that elemental Hg will pass through a wet scrubber system with little or no removal being effected. Therefore, it is important, in order to obtain a high total Hg removal, to study methods that might result in a removal of gaseous, elemental Hg from a flue-gas stream. In this regard, we have been studying the effect of dilute halogen-containing solutions on elemental Hg in gas streams of various compositions. In particular, the results of passing Hg through bubblers containing solutions of iodine, chlorine, and chloric acid are described. Mercury found in the bubbler solutions is an indication of the extent of reaction (oxidation) of elemental Hg with the halogen species, since we have found very little Hg transferred to the liquid phase when only distilled water is used in the bubblers. Results using commercial iodine, sodium hypochlorite, and NOXSORB™ solutions are presented and discussed.

INTRODUCTION

The 1990 Clean Air Act Amendments designate 189 substances as hazardous air pollutants also called "air toxics." Mercury (Hg) has emerged as one of the air toxics of greatest concern. Mercury has been found in the stack emissions from U.S. power plants [1]. Coal-fired power plants account for the vast majority of the estimated total Hg emissions from all U.S. power plants. Mercury emitted from coal-fired power plants has been found in a variety of chemical forms, including elemental Hg and oxidized Hg compounds, such as mercuric chloride [1]. Highly soluble Hg compounds, such as mercuric chloride, are assumed to be readily removed in a wet scrubber system. However, elemental Hg, because of its very low solubility in water, has been shown *not* to be captured in a laboratory-scale wet scrubber system [2]. Therefore, in order to remove elemental Hg with a wet scrubber system, an additional method must be incorporated into a typical wet flue-gas scrubbing process.

We have been studying methods to oxidize gaseous elemental Hg in a typical flue-gas environment, which includes the presence of other potentially reactive gases in the gas mixture, such as oxygen (O_2), nitric oxide (NO), and sulfur dioxide (SO_2). In this paper, we summarize results of Hg removal found by bubbling various gas mixtures containing elemental Hg through solutions of iodine, chlorine, and chloric acid. Although there are some literature references to reactions of elemental Hg with these reactants, we believe that this is the first study that also includes NO and SO_2 in the gaseous reaction mixture. Results for iodine solutions showed that a very high Hg removal was obtained only when the gas phase mixture consisted of Hg and nitrogen (N_2). When other gases were included in the feed gas mixture, the amount of Hg found in the liquid phase was drastically reduced. With chlorine solutions, a more complex behavior was observed that depended on the feed gas mixture and concentration of chlorine used. Chloric acid solutions were prepared from a commercial NOXSORB™ preparation obtained from the Olin Corporation. These solutions showed a moderate amount of Hg removal (14-27%) for the concentrations studied when only O_2 and N_2 were added to the feed gas mixture. Substantially more Hg was removed (34-70%) when NO was added to the feed gas mixture. Finally, when SO_2 was added to the mixture with NO, a moderate decrease in Hg removal from that observed with NO alone was noted (23-49%). All the results are presented and discussed more fully below.

EXPERIMENTAL SETUP AND PROCEDURES

A calibrated and certified Hg permeation tube from VICI Metronics was used as a constant source of vapor-phase, elemental Hg. The permeation tube was placed in a constant temperature water bath controlled to about $\pm 0.5^\circ C$. Bottled, high purity (99.998%) nitrogen gas flowed around the permeation tube to produce a gas stream with a constant concentration of elemental Hg. This gas stream was then combined with another gas stream containing nitrogen and other gaseous components, including O_2 , carbon dioxide (CO_2), NO, and SO_2 . Carbon dioxide was used as a carrier gas for the NO. Oxygen was used from a laboratory air line without further purification. Carbon dioxide, NO, and SO_2 were used from bottled gases without further purification. Nominal purities for these gases were as follows: CO_2 , 99.5%; NO, >99.0%; SO_2 , >99.98%. Gases were blended and their initial composition checked with the following Beckman instruments: O_2 , Model 755 Oxygen Analyzer; CO_2 , Model 864 Infrared Analyzer; NO, Model 951A NO/NO₂ Analyzer; SO_2 , Model 865 Infrared Analyzer. Typical concentrations of the various gas components were as follows: O_2 , 5%; CO_2 , 15%; NO, 250 ppm; and SO_2 , 1000 ppm. After the feed gas composition had stabilized, a valve was turned to admit the gas mixture to a series of three bubblers, each containing 150 mL of solution. The first bubbler contained the solution to be studied, while the

second and third bubblers usually contained distilled water. Commercial solutions of iodine, chlorine (sold as sodium hypochlorite), and chloric acid (sold as NOXSORB™ by the Olin Corporation) were used without further purification. Each test was performed by allowing the gas mixture to bubble through the bubblers for exactly 30 min. Liquid phase samples from each bubbler were saved for total Hg analysis. Mercury analyses were performed by a standard cold-vapor atomic absorption spectrophotometric method (U.S. EPA Method 7470A, SW-846). Mercury concentrations were determined to $\pm 0.02 \mu\text{g Hg/L}$. Estimated accuracy for this method is $\pm 10\%$.

RESULTS AND DISCUSSION

The purpose of the tests described above was twofold. First, we wanted to study the effects on Hg removal from additions of the gases NO and SO₂ to a Hg-containing gas stream. Second, we wanted to learn about the Hg removal process in regard to gas phase versus liquid phase reaction mechanisms. We realized, after we began testing, that only minimal information on our second objective could be gained from these experiments. We could presume that Hg found in the second bubbler was due to gas phase reactions, assuming that liquid carryover from the first bubbler was negligible. However, the situation in bubbler #1 is more complex. From these tests, we cannot distinguish in bubbler #1 between gas phase reactions inside the gas bubble followed by rapid dissolution of products in the liquid phase, and gas-phase dissolution at the gas-liquid interface followed by rapid liquid-phase reaction.

Before tests were performed with various solutions in bubbler #1, initial baseline tests were carried out with only distilled water in all three bubblers. When no elemental Hg was added to the gas stream, no Hg was found in any of the bubbler solutions. This result demonstrates that our system is free of Hg contamination to the detection limit ($\pm 0.02 \mu\text{g Hg/L}$ or $\pm 0.003 \mu\text{g Hg}$ in 150 mL of water) of the Hg analytical method described above. Such baseline tests were run periodically to ensure that no Hg contamination had built up during the course of testing described in this paper. A second baseline test was performed with Hg added to the feed gas stream, but again with only distilled water in all three bubblers. For this test, amounts of Hg barely above the detection limit ($0.004\text{--}0.005 \mu\text{g Hg}$ in 150 mL) were found in each of the three bubblers. This amount of Hg may be compared with the calculated amount of Hg in the gas stream of $1.9 \mu\text{g}$ for the 30-minute test. This result shows that the amount of Hg removed in this experimental apparatus by using only distilled water is less than 0.3%. Therefore, any amounts of Hg found in the bubblers greater than this baseline amount must be from reactions of elemental Hg with components of the various solutions tested in bubbler #1.

Iodine Solutions

Commercial iodine solutions generally contain potassium iodide as a stabilizer, as well as dissolved iodine. A commercial preparation of 0.100 N iodine solution was diluted to make up various iodine concentrations. Previous experiments in our laboratory had shown that iodine solutions react rapidly with elemental Hg vapor [3] in gas streams containing only Hg and N₂. However, those tests had been performed by using only a gas-phase Hg analyzer to measure the elemental Hg concentration in both the feed and effluent gas streams. The analyzer used in those tests has recently been shown by us to be unreliable for measuring Hg in various complex gas mixtures. The tests reported here are the first ones where Hg in the liquid phase has been analyzed. Using a solution of about 125 ppb iodine in bubbler #1, we found that more than 90% of the gas-phase Hg was in the bubbler solutions when only N₂ and Hg were in the feed-gas stream. When O₂ and CO₂ were added to the gas mixture, Hg removal was reduced to about 6%. Only one test was performed with a higher iodine concentration in bubbler #1 (~250 ppb iodine). This test, for a gas stream containing only Hg and N₂, did not give a result substantially different from the lower concentration test (~81% Hg removal). However, when either NO or SO₂ (or both) were added to the gas mixture, the amount of Hg found in the bubbler solutions went either to zero (for NO and for NO plus SO₂) or close to zero (~1% for SO₂). Iodine solutions were not investigated further in these bubbler tests.

In earlier unpublished work in our laboratory, we found that the concentration of gaseous elemental Hg was substantially reduced simply by passing Hg vapors (mixed with nitrogen gas only) over an agitated iodine solution (~250 ppb). These tests showed that the most likely Hg removal mechanism was a rapid gas-phase reaction between iodine vapors and elemental Hg, probably yielding mercuric iodide. This gas phase reaction is probably why a considerable portion (~35%) of the total mercury found in the liquid phase was found in bubblers #2 and #3. However, as discussed above, we cannot exclude the possibility that some of the Hg found in bubbler #1 is from a liquid-phase reaction at the gas-liquid interface. Indeed, a published report on the reaction of iodine in solution with dissolved Hg stated that "the rate was too fast to measure" [4]. The product of the solution reaction was shown to be mercuric iodide by its ultraviolet spectrum [4]. Therefore, without further modeling studies and knowledge of the rate constants (no experimental data on the gas phase reaction of Hg with iodine could be found in the literature), we cannot specifically analyze how much of each reaction (gas phase versus liquid phase) is responsible for the Hg found in bubbler #1.

We conclude that the reaction of Hg with iodine is extremely rapid in the gas phase. However, the presence of other gases readily interferes with this reaction. Whether this interference is caused only by reaction of iodine with the other gaseous components, or whether another mechanism is responsible for the interference cannot be determined from these tests. In any case, iodine would

not seem to be an attractive option for oxidation of elemental Hg in the presence of gases other than nitrogen.

Chlorine Solutions

Solutions of molecular chlorine (Cl_2) are more complex than those of iodine because of the greater tendency of Cl_2 to disproportionate in aqueous solution to hypochlorous acid and chloride ions. Commercial chlorine solutions are sold as sodium hypochlorite because in alkaline solutions the equilibrium between Cl_2 and hypochlorite ions greatly favors the latter. Nonetheless, because of the various equilibria involved, detectable amounts of Cl_2 will exist both in the gas and liquid phases. Results for the removal of Hg by chlorine solutions appeared to depend both on the composition of the feed gas mixture and, in some cases, on the concentration of the chlorine solution. These results are presented in Table 1 and discussed below.

The results in Table 1 are given as a percentage of the total gas-phase mercury found in the liquid phase of all three bubblers; that is, we calculated the total amount of Hg in the gas phase that passes through the bubblers from the known rate of Hg generation by the permeation tube times the 30 min duration of each test. Then the total Hg in the bubblers is found by simple addition of the amounts found in the individual bubblers (in general, bubbler #3 was not analyzed for Hg unless a significant amount was found in bubbler #2). Finally, the total liquid-phase Hg is divided by the total gas-phase mercury and the result is multiplied by 100%. As can be seen from Table 1, removal of Hg in gas mixtures containing only O_2 and N_2 did not change much for different chlorine solution concentrations. Some literature data are available on the gas phase reaction of Hg with Cl_2 . Recent modelling work has assumed the rate constant to be very small [5]. On the other hand, laboratory experiments have shown conflicting results. Some workers have found this reaction to be slow [6] while others have found it to be relatively fast [7]. Still other work has shown the reaction of Hg with Cl_2 to be surface catalyzed [8]. It appears from these conflicting results that one must be very careful in interpreting data for this reaction. Our data suggest that the rate of reaction between Hg and Cl_2 is not fast, because not much change in Hg removal was observed with increasing chlorine concentration. Our conclusion on the gas-phase reaction of Hg with Cl_2 is that it is slow unless there is an appropriate surface available to catalyze the reaction.

For the gas mixtures containing NO and NO plus SO_2 , Hg removal increased with increasing chlorine concentration. However, the rate of increase differed for the two gas mixtures studied. Addition of NO to the feed-gas mixture appeared to have a definite positive effect on the amount of Hg transferred to the liquid phase, when compared to the removals obtained with only O_2 and N_2 present. An explanation for this behavior might be that NO reacts with Cl_2 to yield nitrosyl chloride (NOCl). This reaction has been described in the literature and appears to occur rapidly at room temperature [9]. Although we could not find a literature reference to the reaction of NOCl with elemental Hg, there was a paper which found that NOCl oxidizes mercurous chloride to mercuric chloride as well as oxidizing elemental zinc and copper [10]. Our conclusion for the reaction of Hg in the presence of NO is that NOCl probably reacts faster with Hg than Cl_2 does.

Also, as can be noted in Table 1, when SO_2 is added to the feed-gas mixture, Hg removal is much lower at the lower chlorine concentrations than when SO_2 is not present. However, at the highest chlorine concentration studied, the Hg removal performance with SO_2 present actually slightly exceeded performance without SO_2 . It is well-known that sulfite ions will reduce molecular halogens to their corresponding halides. Because of this reaction, it is hard to understand how the presence of SO_2 could actually increase the oxidation of Hg by Cl_2 . Perhaps the improvement in Hg removal with chlorine concentration can be understood as simply being caused by the presence of an excess of Cl_2 that swamps the reaction between dissolved bisulfite (from absorbed SO_2) and Cl_2 and/or hypochlorite ions in solution.

Plotted in Figure 1 is a graph of the fraction of Hg found in the liquid phase as a function of the logarithm of the initial chlorine concentration in bubbler #1. The data for the tests with NO and no SO_2 in the feed gas mixture are shown with a straight line fit, while the data for the tests with NO and SO_2 in the feed gas mixture are shown with a power curve fit. The curve fits are only a guide to show the difference in the removal dependencies with chlorine concentration for the two gas mixtures. A fuller understanding of this behavior will require more detailed testing.

Chloric Acid Solutions

Chloric acid solutions (HClO_3) were prepared from concentrated NOXSORBTM solutions. Concentrated NOXSORBTM, sold by the Olin Corporation, has a nominal composition of 17.8% HClO_3 and 22.3% sodium chlorate. Tests with two different HClO_3 concentrations were performed: 0.71% HClO_3 (25:1 dilution of the concentrated stock solution) and 3.56% HClO_3 (5:1 dilution). The primary vapor-phase species above these solutions is thought to be chlorine dioxide (ClO_2). However, ClO_2 is very reactive and readily photolyzes to Cl_2 and O_2 . Also, in the presence of moisture, ClO_2 can produce a number of different chlorine oxyacids, such as HOCl , HClO_2 , etc. Therefore, a large number of different species may be present in the vapor above a HClO_3 solution. To the best of our knowledge, the reaction of Hg with either ClO_2 or chlorate anions has not been studied previously. Results of our tests with two different chloric acid concentrations are shown in Table 2.

From the results shown in Table 2, we first note that the change in Hg removal from a solution of 0.71% HClO_3 concentration to Hg removal from an HClO_3 solution with about a five times higher concentration is about the same for each of the three different feed-gas mixtures; that is, Hg

removal was about a factor of two higher with the higher concentration HClO_3 solution. Next, we note that gas mixtures which contained NO showed a higher Hg removal than the gas mixture without NO. This result is similar to that observed with chlorine solutions. However, in this case, a mechanism different than that proposed for Cl_2 is probably responsible. It has been postulated that reaction of NO with NOXSORB™ solutions produces hydrochloric and nitric acids among its products [11]. Because nitric acid dissolves liquid elemental Hg, we propose that this gaseous nitric acid by-product causes the improved Hg removal when NO is present in the gas stream. Contrary to the behavior observed with chlorine, we found that for both concentrations studied, the presence of SO_2 in the feed-gas stream reduced the Hg removal by about 30% from the level without SO_2 but with NO. Also in contrast to the behavior observed with Cl_2 solutions, it appears as though the mechanism that causes a reduction in Hg removal when SO_2 is present cannot be overcome with higher HClO_3 concentrations. This result again points to the possibility that a mechanism different from Cl_2 oxidation of Hg is operating for these HClO_3 solutions. These tests with HClO_3 suggest that the gas-phase reaction of Hg with nitric acid might be rapid and should be examined further.

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TABLES

Table 1. Summary of Hg removal results for tests with chlorine solutions (Cl) in bubbler #1

Feed Gas Composition	Hg removal from Cl solution (%)		
	2.5 ppm Cl	250 ppm Cl	2500 ppm Cl
$\text{O}_2 + \text{N}_2$	12	14	9
$\text{O}_2 + \text{N}_2 + \text{NO} + \text{CO}_2$	19	42	60
$\text{O}_2 + \text{N}_2 + \text{NO} + \text{CO}_2 + \text{SO}_2$	0.5	14	66

Table 2. Summary of Hg removal results for tests with HClO_3 solutions in bubbler #1

Feed Gas Composition	Hg removal from HClO_3 Solution (%)	
	0.71% HClO_3	3.56% HClO_3
$\text{O}_2 + \text{N}_2$	14	27
$\text{O}_2 + \text{N}_2 + \text{NO} + \text{CO}_2$	34	70
$\text{O}_2 + \text{N}_2 + \text{NO} + \text{CO}_2 + \text{SO}_2$	23	49

FIGURE

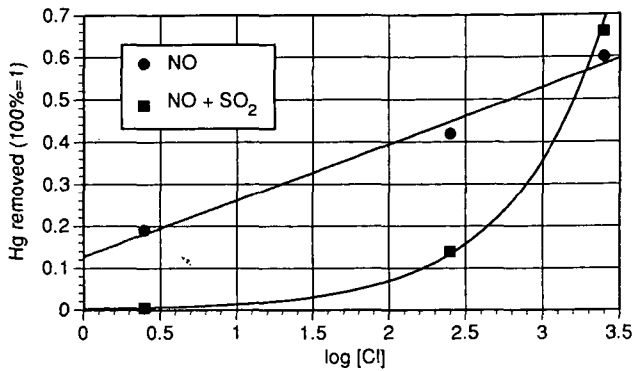


Figure 1. Dependence of Hg removal on the logarithm of the chlorine concentration for two different feed-gas mixtures

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